GULF CANADA LIMITED

RESEARCH AND DEVELOPMENT DEPARTMENT
SHERIDAN PARK, ONTARIO, CANADA

"EVALUATION OF STEAM ADDITIVES AND CLAY STABILIZERS FOR ENHANCED HEAVY OIL RECOVERY PROCESSES"

By

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OBJECTIVE

The objective of this research program is to assess the effect of a number of steam additives and clay stabilizers on the recovery of heavy oils.

Frequently, heavy oil recovery processes fail to produce at commercially acceptable rates due to low displacement efficiency and impaired reservoir permeability, thus reducing the energy available to Canadian industry. This project elucidates the role of selected steam additives and clay stabilizers in enhancing the recovery efficiency of heavy oils and maintaining reservoir permeability.

It is believed that a greater understanding of the phenomenological mechanisms will allow the industry to make better steam additives and clay stabilizers. This, in turn, will permit production of greater proportions of the oil-in-place.

This study compares the performance of several classes of interfacially active steam additives with typical Saskatchewan and Alberta reservoir fluids and core materials. Evaluating the effect of clay stabilizers (i) in preserving permeability, (ii) in enhancing fluid injectivity (iii) in maintaining oil productivity, and (iv) studying their interactions with steam additives are other goals of the study.

Specific areas of study include:-

- Effect of interfacially active steam additives and effect of clay stabilizers on the permeability of preserved cores from Saskatchewan and Alberta heavy oil reservoirs.

- Role of interfacial tension reduction, of steam additives, in enhancing heavy oil recovery.
- Assessment of heavy oil recovery improvement due to the application of steam additives and clay stabilizers using core displacement tests.
- Examination of the flocculation/deflocculation mechanism of particles in the presence of clay stabilizers.
- Comparative testing of the influence of clay stabilizers on the migration of fines.
- Investigation of the compatibility of steam additives and clay stabilizers.

JUSTIFICATION

At present, there are over 50 thermal recovery projects operating in Western Canada. Very few non-thermal projects, such as mine-assisted recovery or caustic flooding, are under planning and/or operation. Steam recovery processes, which include cyclic steam injection and steamflooding, lead all thermal recovery methods with probably about 70% of all in-situ heavy oil production.

Despite the success and popularity of steam injection, there are some problems inherent in its application. Poor vertical sweep efficiency and low displacement efficiency from the hot water zone are two well known major problems. The poor vertical sweep efficiency is due to gravity segregation which leads to early steam breakthrough. Methods designed to improve the vertical sweep efficiency rely mainly on the in-situ formation of foams to reduce the mobility of the injected steam. Methods of enhancing the displacement efficiency from the hot water zone, on the other hand, rely on using inorganic and organic chemical additives which are still the subject of numerous investigations. At present the use of caustic additives at steam temperatures is surrounded with controversy due to excessive reaction with reservoir rock. Organic interfacially active agents, on the other hand, offer much greater flexibility and can be tailored to a wide range of conditions.

The main function of most interfacially active steam additives is to reduce the oil-water interfacial tension to a value low enough to mobilize residual oil. Other interfacially active steam additive, such as the class of compounds termed Thin Film Spreading Agents (TFSA), are presumed to aid in oil displacement through water-oil emulsion destabilization, favorable wettability changes and reduction of viscosity of the oil-water interfacial layer. Significant improvements in oil recovery, due to the application of these additives, have been reported in a number of pilots in the United States. Very little work has been done to assess potential benefits of these additives with Canadian heavy oils.

Another problem with steam recovery methods is that they are often applied, as in many Canadian formations, in low temperature, unconsolidated, shallow geological laydowns which are frequently characterized by high concentrations of clay minerals. When exposed to steam, clays may swell and/or migrate to cause severe matrix permeability reduction and low reservoir depletion efficiency. Thus effective clay mineral control can play an important role in enhancing the steam recovery of heavy oils. Despite this well known fact, little research has been carried out in Canada to assess the value of applying recently developed clay stabilizer formulations in heavy oil reservoirs. In particular a number of cationic polymers have been recently shown to be superior to early inorganic formulations as they offer nearly permanent protection against the swelling and migration of clays. Furthermore, there is no data available on the interactions and compatibility of these clay stabilizers with interfacially active steam additives.

SUMMARY

A laboratory study of the effect of commercial steam additives and clay stabilizers on heavy oil recovery has been undertaken. Three interfacial steam additives and three clay stabilizing agents have been evaluated in the study. The interfacial additives are: Amerigo's reservoir stimulation chemical "Oilflo TCH 956", Baker's Thin Film Spreading Agent "Thermoflood 906", and Surpass Chemicals' petroleum sulfonate surfactant "TRS 410". The three clay stabilizers are: Halliburton's mineral fines and clay stabilization agent "CLA-STA FS", Baker's clay stabilizer, "Thermoflo 106W", and potassium hydroxide.

The three interfacial steam additives produced a comparable, marginal but statistically significant, improvement in oil recovery. Within the range of experimental conditions, the effect of additive concentration on oil recovery was insignificant.

While higher temperatures resulted in an expected increase in oil recovery, temperature-additive interactions were largely negligible. Treatment of clay-sand mixture cores with the clay stabilizers resulted in a small improvement of the oil recovery characteristics, except the case of "Thermoflo 106W" where oil recovery was adversely affected.

With few exceptions, the interfacial steam additives and the clay stabilizers resulted in some permeability reduction of the preserved cores. The most favourable interactions were those of "CLA-STA FS" and KCl. The clay stabilizer "Thermoflo 106W" showed again unfavourable interactions, particularly with a W. Edam (Saskatchewan) preserved core.

The interfacial tension of Pelican Lake (Alberta) and W. Edam (Saskatchewan) oils exhibited a large decrease with time in the presence of saline solutions of the petroleum sulfonate additive "TRS 410". The age of the additive solution had also a pronounced effect on IFT. The other two interfacial additives, TCH 956 and Thermoflood 906, had an insignificant effect on IFT in the range of concentrations studied.

Based on the general settling trends, CLA-STA FS was the most effective in promoting the flocculation of clay particles. Thermoflo 106W, on the other hand, showed unfavourable characteristics.

CONCLUSIONS AND RECOMMENDATIONS

The effect of three commercial interfacially active steam additives and three clay stabilizing agents on the recovery of two heavy oils, from Alberta and Saskatchewan, has been studied under laboratory conditions. The following main conclusions and recommendations have been reached on the basis of the experimental results:-

- All of the examined steam additives resulted in a reduction of Pelican Lake and W. Edam preserved core permeability. The reduction amounted to as much as 70% of the originally measured value. In some of the cases, a partial recovery of the original core permeability was achieved by flowing synthetic formation water after the additive solution.
- The most pronounced interactions with preserved cores, as manifested by permeability reduction and scatter of flow data, were those of the sulfonate additive TRS-410. This can be attributed to adsorption and possible foaming effects of the additive.
- A loss of the original Pelican Lake and W. Edam cores permeability was also observed during clay stabilizers flow. Only during flow of KCl that an improvement of core permeability was observed. Solutions of CLA-STA FS exhibited relatively favourable effects on the permeability of both the W. Edam and Pelican cores. Thermoflow 106W, on the other hand, had an adverse effect on permeability. It resulted in nearly an order of magnitude reduction in the permeability of a W. Edam core.
- Marginal improvement of oil recovery, over brine injection, was obtained by injecting additive solutions. Analysis of the data, nevertheless, proved this small improvement to be statistically significant. The three steam additives had

comparable effects on oil displacement. Only a slight advantage was observed for using "TRS-410" with the W. Edam oil, and for "Thermoflood 906" with the Pelican Lake oil.

- Increased temperature had the expected effect of increasing oil recovery and decreasing the water-oil ratios of W. Edam oil. The effect was insignificant with the Pelican Lake oil due to its relatively low viscosity. No general interaction effects between the temperature and additive type were reflected on oil displacement, except for a small decline in the performance of "Thermoflood 906" at 250°C.
- In the range of experimental conditions, additive concentration had a negligible effect on oil displacement.
- Displacement tests using synthetic clay-sand mixture cores showed CLA-STA FS and KOH to have favourable effects in reducing water retention by the clay and in improving oil recovery. In agreement with the observed poor permeability interacitons, treatment with "Thermoflo 106W" had an adverse effect on oil recovery.
- A significant decrease of interfacial tension, of both Pelican Lake and W. Edam oils, was observed with the petroleum sulfonate additive "TRS 410" solutions. It was found that the age of an oil drop and the age of the additive solution have significant effects on IFT. Thus, a large decrease of IFT with time was measured after injecting an oil drop into "TRS 410" solutions. Aging of the additive solution, on the other hand, resulted in increased IFT. The concentration of "TRS 410" had a less significant effect on IFT.
- The additive "TCH 956" was found to have little effect on IFT, of both Pelican and Edam oils, even at concentrations as high as 500 ppm. This contradicts the manufacturer's claim that one of the mechanisms of oil recovery enhancement, by this additive, is attributed to its ability

to lower interfacial tension. The thin film spreading agent "Thermoflood 906" had also negligible IFT reduction characteristics. This class of additives, however, is known to enhance oil recovery by mechanisms other than IFT reduction.

- The clay stabilizing agent CLA-STA FS was found to be the most effective additive in promoting the flocculation and settling of particles. The performance of CLA-STA FS in the displacement and settling experiments indicates that this clay stabilizer is effective with both swelling and migrating clays.
- Poor settling characteristics of swelling and migrating clays (bentonite and illite) were observed with "Thermoflo 106W" solutions.
- Migration of fines tests indicated a slight decrease in the concentration of discharged fines after treatment with each of the three clay stabilizers.
- The "TRS 410" sulfonate additive exhibited promising IFT characteristics and oil displacement results. Other synthetic sulfonate compounds, alpha olefin and alkylaryl sulfonates, may offer an advantage in terms of their thermal stability and are worth investigating.
- The thin film spreading agent "Thermofloow 906" produced a marginal improvement in oil recovery in the present study. Earlier investigations of these materials, in the open literature, indicate mixed results. An evaluation of a range of different formulations of this class of compounds with a variety of heavy oils is recommended.
- Displacement experiments using preserved cores are recommended, to shed additional light on additive-core material interactions.

- A limited number of displacement experiments involving clay stabilizers have been carried out under the present program. Additional statistically designed series of experiments are required to more fully assess their effect and their interactions with the interfacial steam additives.
- Interfacial tension measurements at elevated temperatures are recommended, as they would more closely approximate steam conditions.
- It may be useful to revise the migration of fines tests in such a way as to improve the sensitivity of the tests to additive treatment.
- The experiments detailed in this research program are recommended as screening tests for selecting additives for field applications.
- The results of this study suggest that the effect of additives on permeability should not be overlooked. The need for developing additives with better interactions with the reservoir rock and minerals is apparent.
- Interfacial tension reduction is a well recognized mechanism for enhancing oil recovery. In addition to exploiting other recovery enhancement mechanisms, there is a need for developing additives capable of achieving an IFT reduction down to the range of 10^{-3} mN/m.

PART I: BACKGROUND

1. LITERATURE REVIEW

Bitumen has an extremely low mobility, such that primary production accounts for a very small fraction of its ultimate recovery from heavy oil reservoirs. Steam injection methods, either in the cyclic stimulation or drive mode, have been employed to improve the recovery of heavy oils (8-16°API) for many years. They currently account for about 75-80% of all EOR production in Canada and the United States.

In spite of the proven success of steam injection methods, substantial amounts of oil are often left behind the injected steam. A variety of additives have been suggested, for injection with steam, to maximize heavy oil recovery. These additives include foaming agents, volatiles and solvents, as well as surfactants and other interfacially active substances.

1.1 Foaming Agents

For almost two decades, and until recently, methods of maximizing oil recovery by steam injection have concentrated on the problems of reservoir conformance and poor vertical sweep efficiency. Attempts, thus, have been made to use foaming agents to help in distributing the heat, of the injected steam, uniformly across the productive intervals of a reservoir (1, 2).

The foam process was apparently first suggested, in connection with waterflooding, by Bond et al in 1958 (3). It has since been extensively investigated (4 - 12). It was not till the mid 1970's, however, when more attention was directed to studying the foaming agents in connection with steam injection processes, and to evaluating the effectiveness of foams at elevated temperatures (1, 2, 14 - 18).

It is believed (13) that possible beneficial effects of foaming additives are derived from three basic mechanisms. First, foam is relatively low-density material which can easily overcome gravitational effects. It can, therefore, act as a diverting agent which reduces the well known gravity override of steam. Secondly, as a blocking agent, foam can be applied to selectively reduce the permeability of high permeability zones in a heterogeneous reservoir. The third mechanism is based on using foam as a mobility control agent. In this mechanism the mobility of injected steam is reduced by the generation of in-situ foam, resulting in an improved displacement efficiency.

In a Midway-Sunset field demonstration (2), a year-long injection of foam with steam resulted in an estimated 30,000 bbl and 50,000 bbl improvement in oil recovery, from the pattern wells and wells outside the pattern respectively. Diversion of steam was believed to have been achieved by three-phase flow and some foam type of activity. It was also suggested that a viscosity increase, in the flowing-steam phase, resulted in enhancing the volumetric conformance. The dominant effect, however, was attributed to a chemical-additive-augmented steam drive in which oil recovery is enhanced by improved emulsification, lowered interfacial tension, and entrainment of the oil in the flowing steam and hot-water phase.

Presently, the effect of foam plugging in enhancing oil production appears to be highly contraversial (19). It is argued that laboratory results which predict the performance of foam with steam, e.g. (20), are irrelevant to reservoir conditions. Some field results which show significant increase in oil production (20) are also discounted (19), on the grounds of being a continuation of a trend that was initiated months before the injection of steam. Furthermore, doubt has also been cast (19) on the in-situ formation of foams in the presence of steam. This is based on the fact that the foam process requires the presence of a very high liquid volume fraction (5×10^{-2}) to cause maximum pressure increase. At 5% quality 200 pound steam has a liquid volume fraction of only 5×10^{-4}, which would not be sufficient to form effective foam.

1.2 Volatile Additives

Another recovery enhancement technique is based on the use of volatiles such as solvents (22, 23), gases (24 - 26), and mixtures of gases and solvents in combination with steam. The use of these additives is supposed to further such beneficial mechanisms as creating initial conductivity to steam, lowering the viscosity of oil, promoting oil swelling, solution gas drive and gas expansion drive.

The majority of laboratory tests and numerical simulation studies indicated a good potential for these additives (27). Generally an acceleration of oil recovery and small increase in total produced oil have been predicted (26, 28, 29). With the very limited testing to-date, the viability of these processes has yet to be established, particularly in view of the present economic environment.

1.3 Alkaline Additives

It is well established that injection of alkaline solutions, into an oil reservoir, leads to in-situ generation of surfactants. The generation of surfactants is due to chemical reactions between the alkaline substance and the organic acids present in the crude oil. The presence of surfactants, in turn, results in a number of beneficial mechanisms; such as emulsification, interfacial tension reduction, and favorable wettability changes. We have recently completed an extensive cost-shared study (30) to assess the alkaline waterflooding process for heavy oils. A detailed review of the process, evaluation of the mechanisms involved, and assessment of its potential may be found in that study.

While alkaline additives have shown promising results in low temperature waterflooding conditions (30 - 32), they had little success when applied with steam in laboratory (33) or field tests (34). Their lack of success appears to be mainly due to excessive reaction with the reservoir rock matrix at steam temperatures. Even at room temperature, significant reaction and alkali consumption was observed (30).

1.4 Interfacially Active Agents

With the controversy surrounding the application of foaming agents and alkaline solutions, as steam additives, increasingly more attention is being directed to the use of other interfacially active agents. There is a vast number of chemicals which have been suggested, and belong to this category. In this group, we include substances which share with alkalis and foams the fact that their function is based on interfacial activity. The mechanisms involved, however, are distinctly different.

Thus, in contrast with alkalis, there is no in-situ generation of surfactants. Also, unlike alkaline additives, which are known to undergo vigorous chemical reactions with the reservoir rock, these substances have low reactivity with the rock. In fact, there is evidence that the reactivity, of some of these materials, decreases at higher temperatures (35, 36). Furthermore, unlike the foaming agents, the blocking and mobility control properties, of most chemicals under this category, are largely insignificant.

The main function of this category of interfacially active steam additives is to enhance the displacement efficiency from the hot water zone. One or more of a variety of mechanisms is supposed to play a role in the efficiency improvement. These mechanisms include oil-water interfacial tension reduction, water-in-oil emulsion destabilization, emulsification and entrainment of oil, favorable wettability changes, and reduction of the viscosity of the oil-water interfacial layer.

Among the additives of current interest to heavy oil recovery are petroleum sulfonates, alpha olefin sulfonates, and synthetic alkylaryl sulfonates. Petroleum sulfonates have been shown, in laboratory displacement tests, to substantially improve oil recovery and reduce residual bitumen saturations (37). Some concern over the thermal degradation of petroleum sulfonates and their loss during laboratory displacements was expressed in that study. Another study (38) predicted the improvement in steamflood oil recovery, due to the application of sulfonate additives, to reach about 8 to 32% for a Kern River-type reservoir. In the latter study, it was also demonstrated that the alpha olefin and synthetic alkylaryl sulfonates exhibit sufficient thermal stability to enable their use as steam additives. Comparative evaluation of a number of steam additives (38) gave further evidence of the superiority of sulfonate additives for bitumen recovery.

Several recent publications and patents (39 - 46) deal with a special class of interfacially active steam additives, termed Thin Film Spreading Agents (TFSA). Substantial increases in heavy oil recovery, as a result of applying these non-ionic additives, have been reported. For example an extensive statistical study (46) reported the production cycle histories of 44 wells which received similar steam and TFSA chemical treatments. The results indicated an incremental oil production in the treated cycles of up to 85%. The effectiveness of these compounds has been attributed (47) to their ability to displace thick films forming at the interfaces between crude oil and the reservoir rock and water phases. In place of the thick flow-resisting films, very thin mobile films, which offer little resistance to coalescence and water-wetting of rock, are formed. This mechanism, essentially, amounts to destabilization of water-in-oil emulsions and favorable wettability changes. The selection of the most effective TFSA compound, for actual complex reservoir conditions, may involve a compromise between the most effective spreading agent for the rock-oil interface and the most suitable compound for the rock-connate water-oil interface (40). The importance of selecting the optimum TFSA composition, for a specific oil/water/rock system, is highlighted by the difference in the degree of success obtained with these compounds in the laboratory. For example, while one of the TFSA compounds resulted in up to 30% improvement in laboratory synthetic core flooding tests (48), another formulation (Thermoflood 808) was reported (38) to have no effect on laboratory bitumen recovery under flooding or drawdown conditions.

A range of other additives and patented compositions is available on the market for the enhancement of heavy oil recovery in steam stimulation and steamflooding projects. A widely publicized patented surfactant is Amerigo's "Oilflo TCH 956". According to the manufacturer (49), the primary benefit of this stimulation chemical is its ability to reduce the viscosity and surface tension of heavy oil. Application of this additive has been claimed to have resulted in very large oil production increases in Venezuela, California, Lloydminster and Cold Lake field trials.

1.5 Clay Stabilizers

Clay mineralogy problems in oil recovery have long been recognized as a major cause of reduced permeability and declining oil productivity (50). The clay problems are compounded in heavy oil reservoirs which are often characterized by high concentrations of clay minerals in poorly consolidated shallow geological laydowns.

According to the popular views on clay damage (51), these minerals are generally classified as swelling and migrating clays. Swelling clays (such as montmorillonite) tend to exchange loosely bound cations, e.g. sodium, for water resulting in clay expansion. Migrating clays (such as kaolinite and illite) are not strongly cemented in the formation and are easily dispersed by the flowing fluids. Dispersed fines become entrained in the moving fluids until points of lodgement (pore throats) are encountered or until bridging occurs. This phenomenon can result in a drastic decrease of permeability and oil productivity. Swelling of clays, which may also be accompanied by the release of migrating silica and clay fines, is another important cause of declining permeability as well as reduced fluid injectivity.

In general, the damage potential of clay minerals is related to their cation exchange capacity, structural orientation, and geological laydown patterns as well as the existing cation environment. The extent of clay damage depends on the relative combined strength of clay particles dispersion forces (e.g. hydration of exchangeable cations, repulsion of exchangeable cation atmospheres, mechanical sheer) and the combined strength of clay particles binding forces (e.g. van der Waals forces, electrostatic attractions, sorption of ions between adjacent layers, sorption of organic matter from oil).

Formulations applied as clay stabilizing agents generally contain multi-sited cationic chemicals. Early formulations employed calcium, ammonium or hydrogen ions, which are relatively inactive, to replace the more active sodium ions. These early formulations constituted only temporary protection measures, as the inactive ions can be quickly counter replaced by the active swelling ions to re-establish the previous state. Polymers with cationic functional groups were found to adsorb on clay platelets and to stabilize the clays much more effectively (52 - 54). They offer nearly permanent protection to clays; for the release of adsorbed polymers requires simultaneous release of ions at numerous sites.

Effectiveness of cationic polymers and other clay stabilization agents under conditions of high temperature steam has been the subject of very limited research (55). Interactions of clay stabilizer with interfacially active steam additives during steam recovery processes is another area which found very little attention and requires much investigation.

1.6 Flow of Polymer Solutions through Porous Media

It has already been pointed out that many of the interfacial steam additives and clay stabilizers are relatively large polymer molecules. These large molecules are known to adsorb on, or otherwise be retained by, the rock surfaces of a petroleum reservoir. The retention of the molecules results not only in a loss of the additive, but also an additional flow resistance. A loss of additive activity and an increased resistance to flow have, obviously, important implications for oil recovery.

According to the widely accepted theories (56 - 61), the effective permeability of a porous medium, to polymer solution flow, is reduced as a direct consequence of the presence of a layer of adsorbed polymer. The presence of the latter amounts to a reduction in the cross-sectional area of the pores in the medium. In addition to the adsorption effect, mechanical entrapment of the polymer molecules by pore constrictions, hydrodynamic retention, and other complex interactions with the reservoir matrix result in a further reduction of the effective permeability. Moreover, viscoelasticity has, also, long been shown to add to increased flow resistance (62 - 65), particularly at high flow rates.

The relative importance of the various mechanisms (direct adsorption effect, mechanical trapping, hydrodynamic retention or other complex phenomena), has been studied by a number of investigators (56, 66). In general, numerous factors play a role in determining the predominant mechanism. These include, the chemical nature of polymer molecules and reservoir rock, molecular size of polymer, concentration of polymer molecules, flow rate, presence of electrolytes, pH of flowing solutions, and pore-size distribution.

PART II - STUDY PROGRAM

2. FLUIDS CHARACTERIZATION

The fluids considered at various stages of this project included two heavy oil crudes from Alberta and Saskatchewan, associated formation waters, several additive solutions and synthetic brine solutions.

Two well-head crude oil samples, and their associated formation water, were obtained from Gulf West Edam area (Saskatchewan) and Gulf Pelican Lake area (Alberta). No field additives were present in any of the samples. The respective wells sampled were:-

- Gulf West Edam Well 5-30-48-20W3
- Gulf Pelican Lake Well 7-8-81-22W4

Solutions of three steam additives and three clay stabilizers, at various concentrations, have been used during the different phases of this study. The selected additives are:-

Interfacial Steam Additives

S1: Amerigo's reservoir stimulation chemical "OILFLO TCH 956"
S2: Baker's Thin Film Spreading Agent "Thermoflood 906"
S3: Surpass Chemicals' petroleum sulfonate additive "TRS 410"

Clay Stabilizers

C1: Halliburton's mineral fines and clay stabilization agent "CLA-STA FS"
C2: Baker's Clay Stabilizer "Thermoflo 106W"
C3: Potassium hydroxide

2.1 Crude Oil Analysis

Several standard ASTM and Gulf analytical procedures have been conducted to determine the basic chemical and physical characteristics of the two heavy crude oils. Tables 2-1 and 2-2 list the analytical results for the two samples.

Further detailed chemical analyses of the two heavy oils have also been carried out, on the basis of mass spectrometry. The Pelican Lake oil was distilled into four fractions, as shown in Table 2-3. The W. Edam oil, on the other hand, was distilled into only three fractions, as the lightest fraction (IBP-200°) contained an insignificant amount of oil, Table 2-4.

The first three (light) fractions of the Pelican Lake oil, and the first two fractions of the West Edam oil, were analyzed by mass spectrometry. The mass spectrometric analyses for the Pelican Lake oil and W. Edam oil are reported in Tables 2-5 to 2-7 and Tables 2-8 and 2-9, respectively.

No mass spectrometric analysis, however, was carried out on the residue fraction (550°C+) in either of the two cases. These heavy fractions are very difficult to analyze by this method. However, previous Gulf R&D experience, with similar heavy fractions, indicates that they largely contain asphaltic components, high molecular weight sulphur compounds, cycloparaffins and polyaromatics.

TABLE 2-1

Pelican Oil Characteristics

		Method*	
Specific Gravity, °API		Calculated	15.1
Density (g/mL)	15°C	D4052-81	0.9648
	65°C	D4052-81	0.9338
Viscosity (cSt)	25°C	D445	715.0
	40°C	D445	251.8
Total Acid Number (mg KOH/g oil)		D664	0.92
Total Base Number		D2896	3.4
Salt Content, ppm		GCM 117	16
Ramsbottom Carbon Residue R.C.R. %		D524	8.03
Pour Point, °C		D97	-24.0
Sulphur, %		D2622	5.92
Mercaptans/H_2S, ppm		GCM 118	253/Nil
Total Nitrogen, ppm		D3228	2825

* **NOTE:** D = ASTM Method
GCM = Gulf Canada Method

TABLE 2-2

W. Edam Oil Characteristics

		Method*	
Specific Gravity, °API		Calculated	13.2
Density (g/mL)	15°C	D4052-81	0.9771
	65°C	D4052-81	0.9462
Viscosity (cSt)	25°C	D445	2585
	40°C	D445	646.9
Water Content, %		D95	2.6
Total Acid Number (mg KOH/g oil)		D664	0.96
Salt Content, ppm		GCM 117	1520
Ramsbottom Carbon Residue R.C.R. %		D524	10.3
Bottoms Sediment & Water		D96	4.2
Pour Point, °C		D97	-15.0
Sulphur, %		D2622	4.12
Mercaptans/H_2S, ppm		GCM 118	1660/Nil
Total Nitrogen, ppm		D3228	2887

* **NOTE:** D = ASTM Method
GCM = Gulf Canada Method

TABLE 2-3

Pelican Lake Crude Fractions

	Fraction #1	Fraction #2	Fraction #3	Fraction #4
BP, °C	IBP-220	220-325	325-550	550+ Residue
Wt %	6.5	14.2	30.2	48.5

IBP, 80°C

TABLE 2-4

West Edam Crude Fractions

	Fraction #1	Fraction #2	Fraction #3	Fraction #4
BP, °C	IBP-220	220-325	325-550	550+ Residue
Wt %	-	14.1	46.8	37.6

TABLE 2-5

Pelican Lake Crude (FR #1, IBP-220°C)
Mass Spectrometric Analysis

Hydrocarbon Type	Z No.	Volume Percent
Paraffins	+2	40.2
Monocycloparaffins	0	46.7
Dicycloparaffins	-2	3.7
Tricycloparaffins	-4	0.0
Mono-olefins	0	2.5
Cyclo-olefins	-2	0.3
Dicyclo-olefins	-4	0.0
Alkylbenzenes	-6	6.4
Styrenes/Indans	-8	0.0
Indenes	-10	0.1
Naphthalenes	-12	0.0
Biphenyls	-14	0.0

TABLE 2-6

PELICAN LAKE CRUDE (FR #2, 220-325°C)
DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

Hydrocarbon Type (Cn.H2n-Z)	Z No.	Determined Volume Percent		
Saturates				71.48
Paraffins	+2	14.52		
Cycloparaffins			56.97	
Noncond Cycloparaffins	0	35.33		
Cond Dicycloparaffins	-2	17.11		
Cond Polycycloparaffins	-4	4.52		
Aromatics				28.07
Monoaromatics			21.41	
Alkylbenzenes	-6	12.96		
Benzocycloparaffins	-8	4.89		
Benzodicycloparaffins	-10	3.56		
Diaromatics			5.20	
Naphthalenes	-12	5.20		
Naphthocycloparaffins	-14	0.00		
Fluorenes	-16	0.00		
Triaromatics			0.15	
Phenanthrenes/Anthracene	-18	0.15		
Phenanthrocycloparaffins	-20	0.00		
Tetraaromatics			0.03	
Pyrenes/Benzofluorenes	-22	0.00		
Chrysenes/Benzanthracene	-24	0.03		
Pentaaromatics			0.00	
Chrysocycloparaffins	-26	0.00		
Benzpyrenes/perylenes	-28	0.00		
Dibenzanthracenes	-30	0.00		
Unidentified			0.00	
Cn.H2n-32	-32	0.00		
Cn.H2n-38/Cn.H2n-26.S	-36	0.00		
Cn.H2n-42/Cn.H2n-32.S	-42	0.00		
Cn.H2n-44/Cn.H2n-34.S	-44	0.00		
Aromatic Sulfur			1.27	
Benzothiophenes	-10S	1.25		
Dibenzothiophenes	-16S	0.02		
Benzonaphthothiophenes	-22S	0.00		

TABLE 2-7

PELICAN LAKE CRUDE (FR #3, 325-550°C)
HEAVY DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

Hydrocarbon Type (Cn.H2n-Z)	Z No.	Mass %
Paraffins	+2	8.11
Cycloparaffins		31.20
Monocycloparaffins	0	10.60
Dicycloparaffins	-2	7.92
Tricycloparaffins	-4	5.21
Tetracycloparaffins	-6	5.11
Pentacycloparaffins	-8	2.00
Hexacycloparaffins	-10	0.36
Monoaromatics		
Alkylbenzenes	-6	5.84
Benzocycloparaffins	-8	5.48
Benzodicycloparaffins	-10	7.82
Diaromatics		
Naphthalenes	-12	7.21
Naphthocycloparaffins	-14	5.31
Fluorenes	-16	4.27
Triaromatics		
Phenanthrenes/Anthracene	-18	4.18
Phenanthrocycloparaffins	-20	2.07
Tetraaromatics		
Pyrenes/Benzofluorenes	-22	1.76
Chrysenes/Benzanthracene	-24	0.57
Pentaaromatics		
Chrysocycloparaffins	-26	0.40
Benzpyrenes/Perylenes	-28	0.21
Dibenzanthracenes	-30	0.02
Unidentified		
Cn.H2n-32	-32	0.75
Cn.H2n-36/Cn.H2n-26.S	-36	0.66
Cn.H2n-38/Cn.H2n-28.S	-38	0.54
Cn.H2n-42/Cn.H2n-32.S	-42	0.40
Cn.H2n-44/Cn.H2n-34.S	-44	0.41
Aromatic Sulfur		
Benzothiophenes	-10S	5.65
Dibenzothiophenes	-16S	3.39
Benzonaphthothiophenes	-22S	0.36
Polar Compounds		

TABLE 2-8

W. Edam Crude (FR #2, 220-325°C)
Distillate Analysis by Low Resolution Mass Spectrometry

Hydrocarbon Type (Cn.H2n-Z)	Z No.	Determined Volume Percent		
Saturates				78.70
Paraffins	+2	15.52		
Cycloparaffins			63.18	
Noncond Cycloparaffins	0	35.87		
Cond Dicycloparaffins	-2	20.39		
Cond Polycycloparaffins	-4	6.92		
Aromatics				20.56
Monoaromatics			16.49	
Alkylbenzenes	-6	8.67		
Benzocycloparaffins	-8	4.79		
Benzodicycloparaffins	-10	3.04		
Diaromatics			3.29	
Naphthalenes	-12	3.29		
Naphthocycloparaffins	-14	0.00		
Fluorenes	-16	0.00		
Triaromatics			0.20	
Phenanthrenes/Anthracene	-18	0.20		
Phenanthrocycloparaffins	-20	0.00		
Tetraaromatics			0.04	
Pyrenes/Benzofluorenes	-22	0.00		
Chrysenes/Benzanthracene	-24	0.04		
Pentaaromatics			0.00	
Chrysocycloparaffins	-26	0.00		
Benzpyrenes/perylenes	-28	0.00		
Dibenzanthracenes	-30	0.00		
Unidentified			0.00	
Cn.H2n-32	-32	0.00		
Cn.H2n-38/Cn.H2n-26.S	-36	0.00		
Cn.H2n-42/Cn.H2n-32.S	-42	0.00		
Cn.H2n-44/Cn.H2n-34.S	-44	0.00		
Aromatic Sulfur			0.53	
Benzothiophenes	-10S	0.53		
Dibenzothiophenes	-16S	0.00		
Benzonaphthothiophenes	-22S	0.00		

TABLE 2-9

W. Edam Crude (FR #3, 325-550°C)
Heavy Distillate Analysis by Low Resolution Mass Spectrometry

Hydrocarbon Type (Cn.H2n-Z)	Z No.	Mass %
Paraffins	+2	
Cycloparaffins		
Monocycloparaffins	0	11.76
Dicycloparaffins	-2	10.16
Tricycloparaffins	-4	7.07
Tetracycloparaffins	-6	5.09
Pentacycloparaffins	-8	1.82
Hexacycloparaffins	-10	0.57
Monoaromatics		
Alkylbenzenes	-6	5.76
Benzocycloparaffins	-8	5.31
Benzodicycloparaffins	-10	7.02
Diaromatics		
Naphthalenes	-12	6.01
Naphthocycloparaffins	-14	5.63
Fluorenes	-16	5.13
Triaromatics		
Phenanthrenes/Anthracene	-18	4.31
Phenanthrocycloparaffins	-20	2.15
Tetraaromatics		
Pyrenes/Benzofluorenes	-22	1.93
Chrysenes/Benzanthracene	-24	0.68
Pentaaromatics		
Chrysocycloparaffins	-26	0.76
Benzpyrenes/perylenes	-28	0.35
Dibenzanthracenes	-30	0.12
Unidentified		
Cn.H2n-32	-32	0.12
Cn.H2n-36/Cn.H2n-26.S	-36	0.49
Cn.H2n-38/Cn.H2n-28.S	-38	0.29
Cn.H2n-42/Cn.H2n-32.S	-42	0.26
Cn.H2n-44/Cn.H2n-34.S	-44	0.01
Aromatic Sulfur		
Benzothiophenes	-10S	3.54
Dibenzothiophenes	-16S	2.12
Benzonaphthothiophenes	-22S	0.61
Polar Compounds		

2.2 Formation Water Analysis

Standard compositional analysis was carried out on formation water samples from the Pelican Lake and W. Edam areas. Table 2-10 shows a typical analysis of formation water from the Pelican lake area. The analysis of a W. Edam formation water sample is given in Table 2-11. It is worth noting that the W. Edam reservoir fluids (crude oil and formation water) have been used in a previous cost-shared study (D.S.S. Contract Serial Number OSQ.84-00094).

2.3 Properties of Additive Solutions

The basic properties of the additive solutions, used throughout this study, are listed in Tables 2-12 and 2-13. Concentrations of the additives have been selected in accordance with the respective manufacturer's recommendation for most field applications, or according to indications in the open literature studies. These concentrations have been consistently used through the course of this project.

For purposes of the interfacial tension study additional steam additive solutions, at different concentrations, were prepared and used. These concentrations were:-

TRS-410:	3000, 5000, 6500, 8000 and 10000 ppm
TCH-956:	25, 50, 125, 250 and 500 ppm
Thermoflood-906:	200, 400, 600, 800 and 1000 ppm

TABLE 2-10

Analysis of West Edam Formation Water Samples

	Sample 5-30-48-20-W3	
Relative Density, 15°C	1.0476	
pH	7.6	
Ion	Conc. g/m^3	Conc. mol/m^3
Na	20599	896
K	427	10.9
Ca	680	17.0
Mg	730	30.0
Fe	0.7	0.013
Cl	37800	1066
HCO_3	673	11.0
SO_4	28	0.291
CO_3	0.0	0.0
H_2S	-	-
Si as SiO_2, ppm	7.5	
Total Dissolved Solids g/m^3 "calculated"	60700	

TABLE 2-11

Pelican Lake
Produced Water Analysis

Component	µg/g
Sodium	1950
Potassium	123
Calcium	3.0
Magnesium	5.8
Iron	<0.2
Chloride	1520
Sulphate	22.7
Carbonate	123
Bicarbonate	2463

TABLE 2-12

Properties of Interfacial Steam Additive Solutions

	Density (g/cm^3) 15°C	Density (g/cm^3) 25°C	Viscosity (cSt) 25°C	pH
S1 TCH 956 (25 ppm*)	0.9996	0.9937	0.92	5.4
S2 Thermoflood 906 (200 ppm*)	0.9995	0.9936	0.91	5.8
S3 TRS 410 (3000 ppm*)	0.9996	0.9937	0.92	7.0

* All solutions in distilled water

TABLE 2-13

Properties of Clay Stabilizer Solutions

	Density (g/cm^3) 15°C	Density (g/cm^3) 25°C	Viscosity (cSt) 25°C	pH
C1 CLA-STA FS (1 vol% in 4 wt% KCl)	1.0249	1.0189	1.11	6.1
C2 Thermoflo 106W (2000 ppm in distilled water)	0.9991	0.9932	0.93	6.9
C3 KOH (15 g/L)	1.0094	1.0034	0.92	12.9

2.4 Compatibility of Additive Solutions with Formation Water

Qualitative compatibility testing of the six additive solutions with the W. Edam and with Pelican Lake formation water has been conducted. The aim of these qualitative tests was to identify potential interaction problems; as may be detected by the formation of precipitates.

In these tests, each of the additive solutions was mixed with an equal volume of formation water (W. Edam and Pelican Lake). With the exception of the potassium hydroxide solutions, no precipitation was observed with any other additive solution. In the case of potassium hydroxide, precipitation was immediately observable. This is expected due to the presence of magnesium ions in the formation water, resulting in the precipitation of the highly insoluble magnesium hydroxide.

3. EFFECT OF ADDITIVES ON PERMEABILITY

As mentioned in the background section, polymer additives generally interact with, and are retained by, the reservoir rock matrix. Adsorption, ionic reactions, and hydrodynamic effects are the main mechanisms involved. Other types of additives, such as caustic solutions, are also known to undergo significant interactions, due to chemical reactions, with the reservoir rock. Permeability reduction is an obvious manifestation of these interactions. Studying the effect of additives on permeability is, therefore, an important element in characterizing their performance.

All of the six additives, three steam additives and three clay stabilizers, were tested with preserved core samples from W. Edam (Saskatchewan) and Pelican Lake (Alberta). Specific fluid flow sequences were consistently used to evaluate the effect of each additive on the permeability of the reservoir core sample.

3.1 Permeability Measurements

The procedure utilized for permeability measurements was as follows:-

- A cylindrical plug (2.5 cm diameter, and 12 to 15 cm long) was subsampled from a preserved core. The cores used for subsampling, belonged to one location in the W. Edam area (Saskatchewan) and another location in the Pelican Lake area (Alberta).

- The cylindrical core sample was mounted in a Hassler-type holder under a confining pressure of 1000-1100 psi. The cell was equipped with a pressure transducer, and a constant-rate pump was used for fluid injection and circulation.

- Preparation of the core sample, for permeability measurements included flushing with toluene followed by pentane. The flushing was continued until the core sample was completely cleaned of the original reservoir fluids. It was then dried with nitrogen.

- The core sample was saturated with synthetic formation water (prepared according to either the Pelican Lake formation water composition or W. Edam composition, depending on the core sample used). The formation water was allowed to flow through for several hours. It was then circulated through the core sample for a period of time ranging from several hours to several days to ensure equilibration.

- Several steady-state pressure drop-flow rate measurements were taken. For each measurement, the formation water was circulated through the core sample until a constant pressure drop was achieved. The flow rate was then accurately determined by weighing a fluid sample collected over a recorded period of time. The permeability of the core sample was calculated by fitting a least squares line, through the pressure drop-flow rate points, according to Darcy's law.

- After the initial measurement of core permeability to formation water, the permeability of the core was remeasured, at steady state, with the additive solution followed by the synthetic formation water once again. Between the different flow steps, at least 20 pore volumes of the new fluid were used to flush the core before taking any flow measurements.

3.2 Effect of Steam Additives on Permeability

Figures 3-1 to 3-8 show all the results of flow measurements on three fresh Pelican core samples, testing one of the three steam additives in each case. In each case, the flow sequence of synthetic formation water before and after an additive solution flow has been consistently followed. The bargraphs 3-1, 3-3 and 3-5 highlight the effect of each additive solution on core permeability, by comparing the measured permeability before, during and after additive flow. The remaining figures, 3-2, 3-4, 3-6 and 3-8, show the experimental flow rate - pressure gradient points, and the least squares fitted line for each set.

Similar to the set of Pelican cores measurements, Figures 3-9 to 3-14 show the results of flow of the three different steam additives with a W. Edam core sample. Again, the figures present detailed experimental flow measurements, and a summary of permeability comparisons given in the form of bargraphs. In this set of measurements, Figures 3-9 to 3-14, a single W. Edam core sample was employed for the three additives. This is the only case, in the permeability study, where a non-fresh core sample was used for consequetive additive solution flow. This variation was tried to obtain a direct comparison of additives on the same core.

As a detailed rheological, additive adsorption and retention examination was not the object of the present study, no attempt has been made to investigate such relationships as shear stress - shear rate or effective hydrodynamic thickness of adsorbed additive. Rather, the maximum flow rate was limited to about 1000 g/h, in all the measurements, and the permeability was estimated in accordance with Darcy's law in this range. Even in

FIGURE 3-1

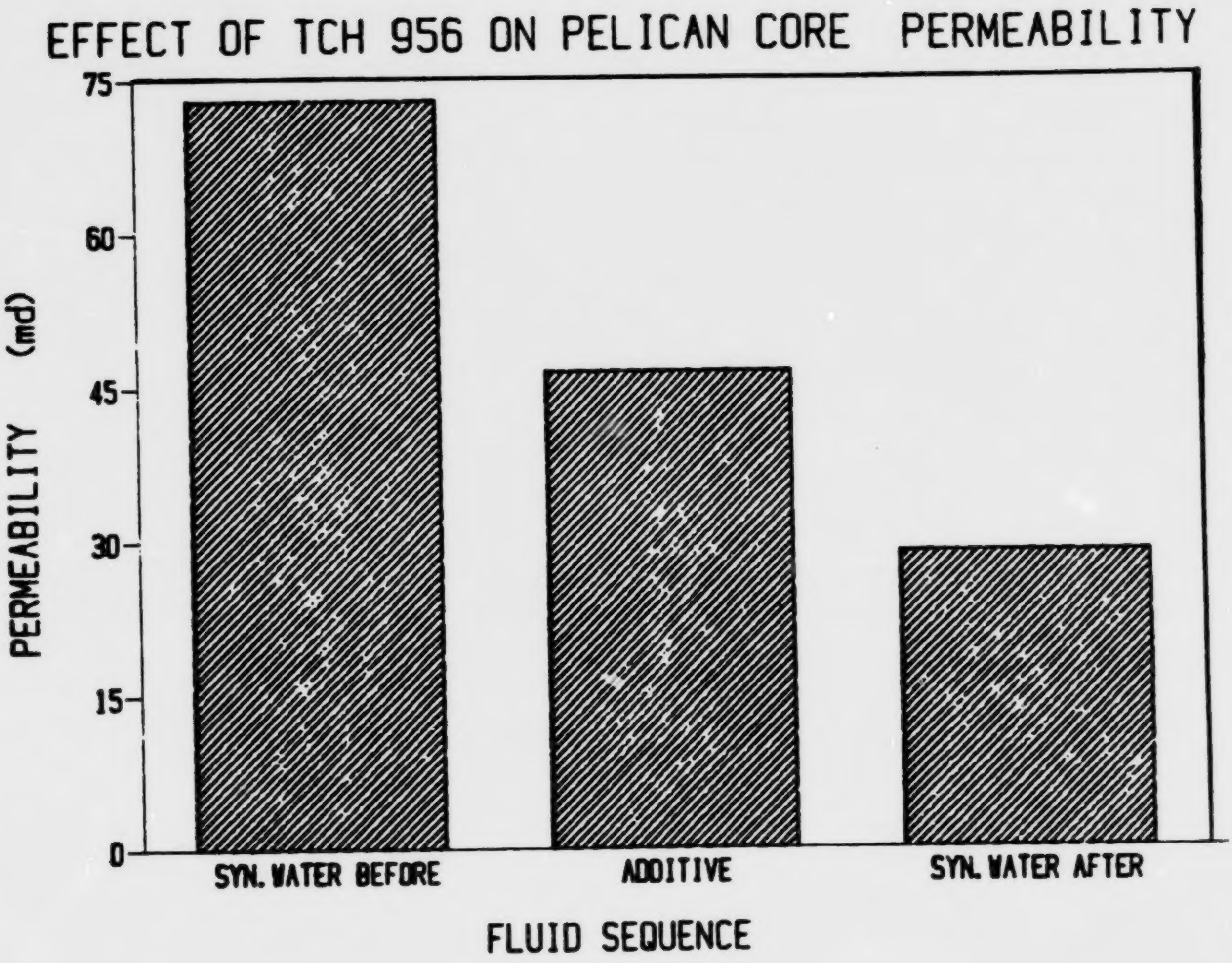

EFFECT OF TCH 956 ON PELICAN CORE PERMEABILITY
75
60
45
30
15
0
PERMEABILITY (md)
SYN. WATER BEFORE
ADDITIVE
SYN. WATER AFTER
FLUID SEQUENCE

FIGURE 3-2

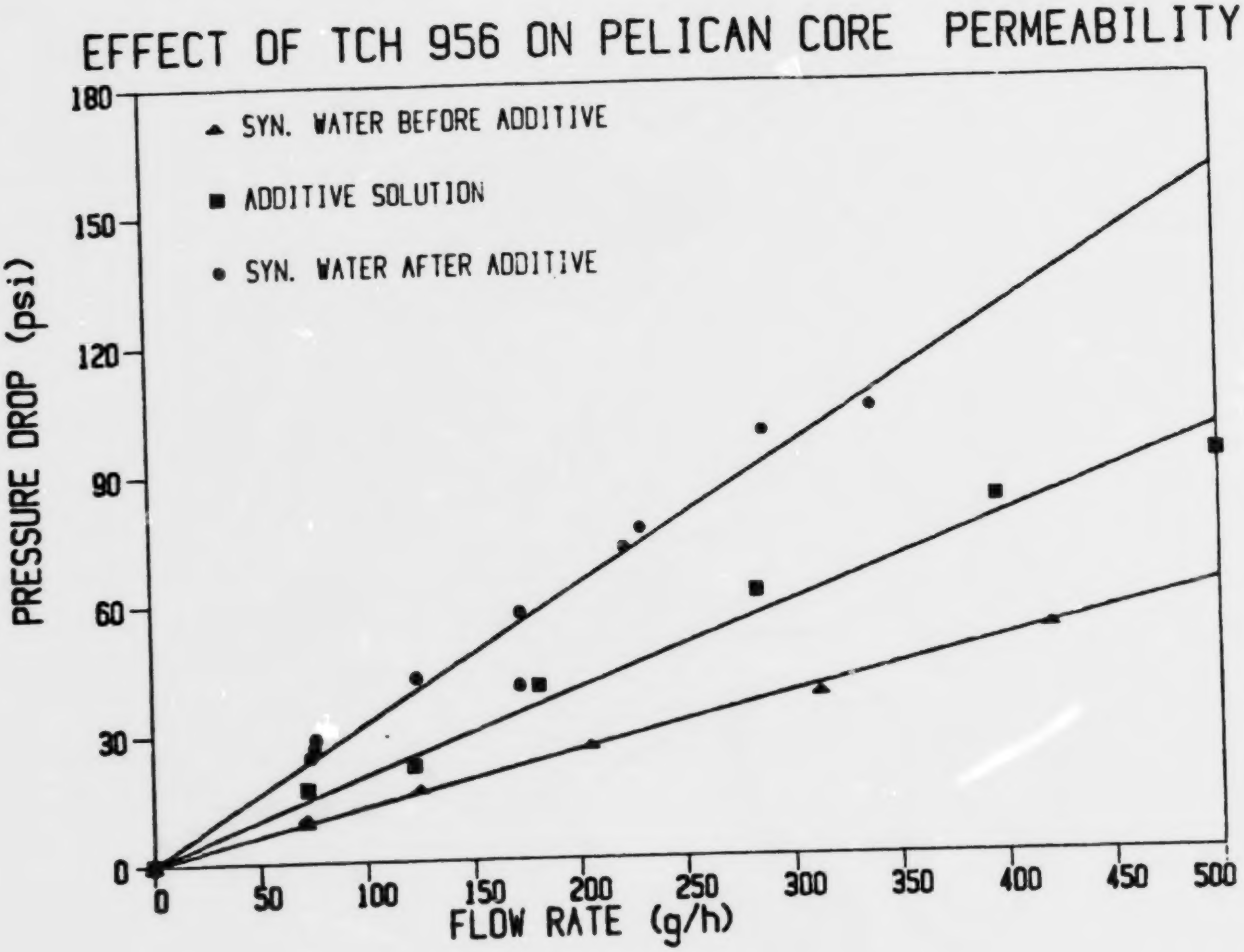

EFFECT OF TCH 956 ON PELICAN CORE PERMEABILITY
▲ SYN. WATER BEFORE ADDITIVE
■ ADDITIVE SOLUTION
● SYN. WATER AFTER ADDITIVE
PRESSURE DROP (psi)
180
150
120
90
60
30
0
0
50
100
150
200
250
300
350
400
450
500
FLOW RATE (g/h)

FIGURE 3-3

EFFECT OF TRS-410 ON PELICAN CORE PERMEABILITY

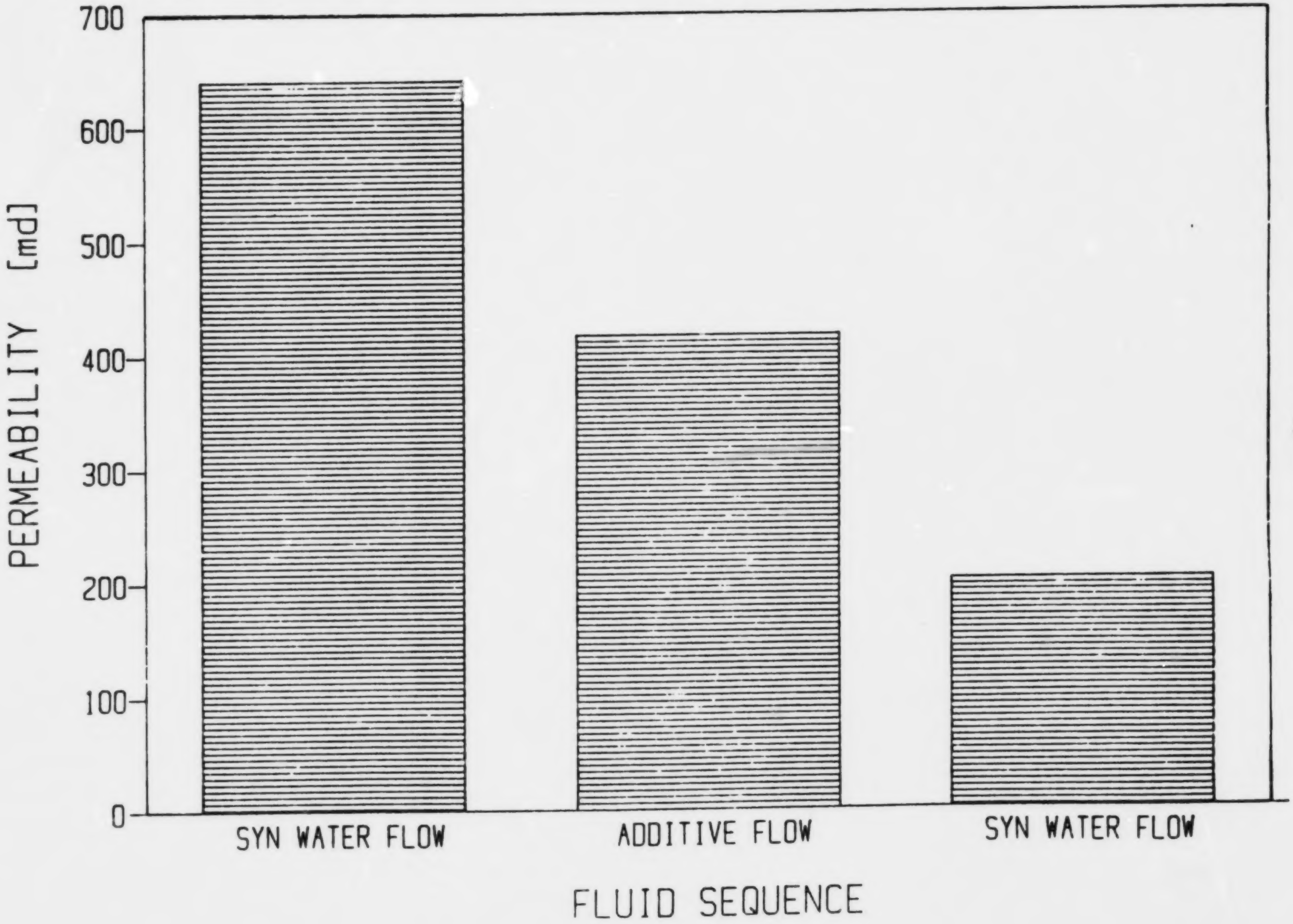


FIGURE 3-4

EFFECT OF TRS-410 ON PELICAN CORE PERMEABILITY

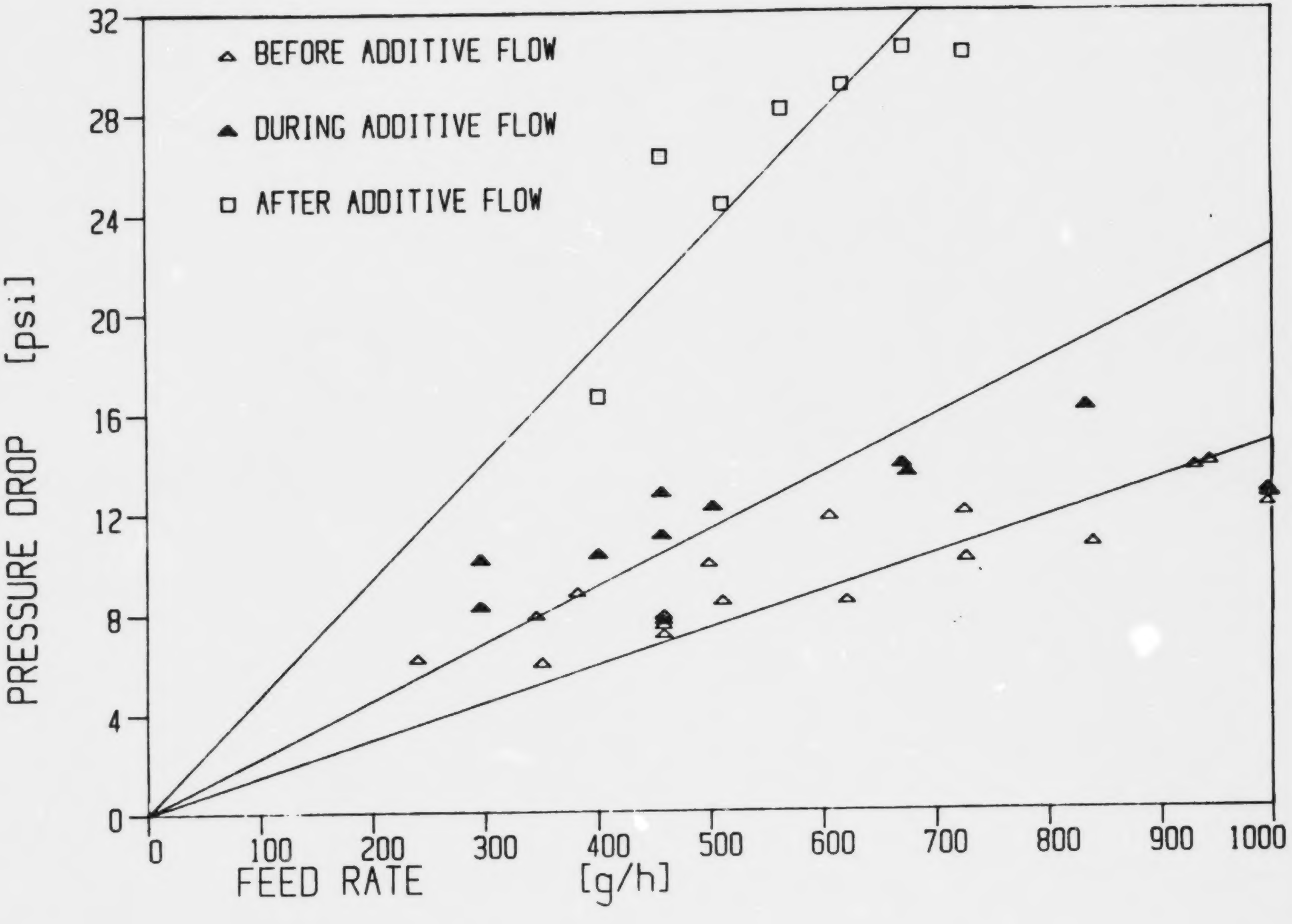


FIGURE 3-5

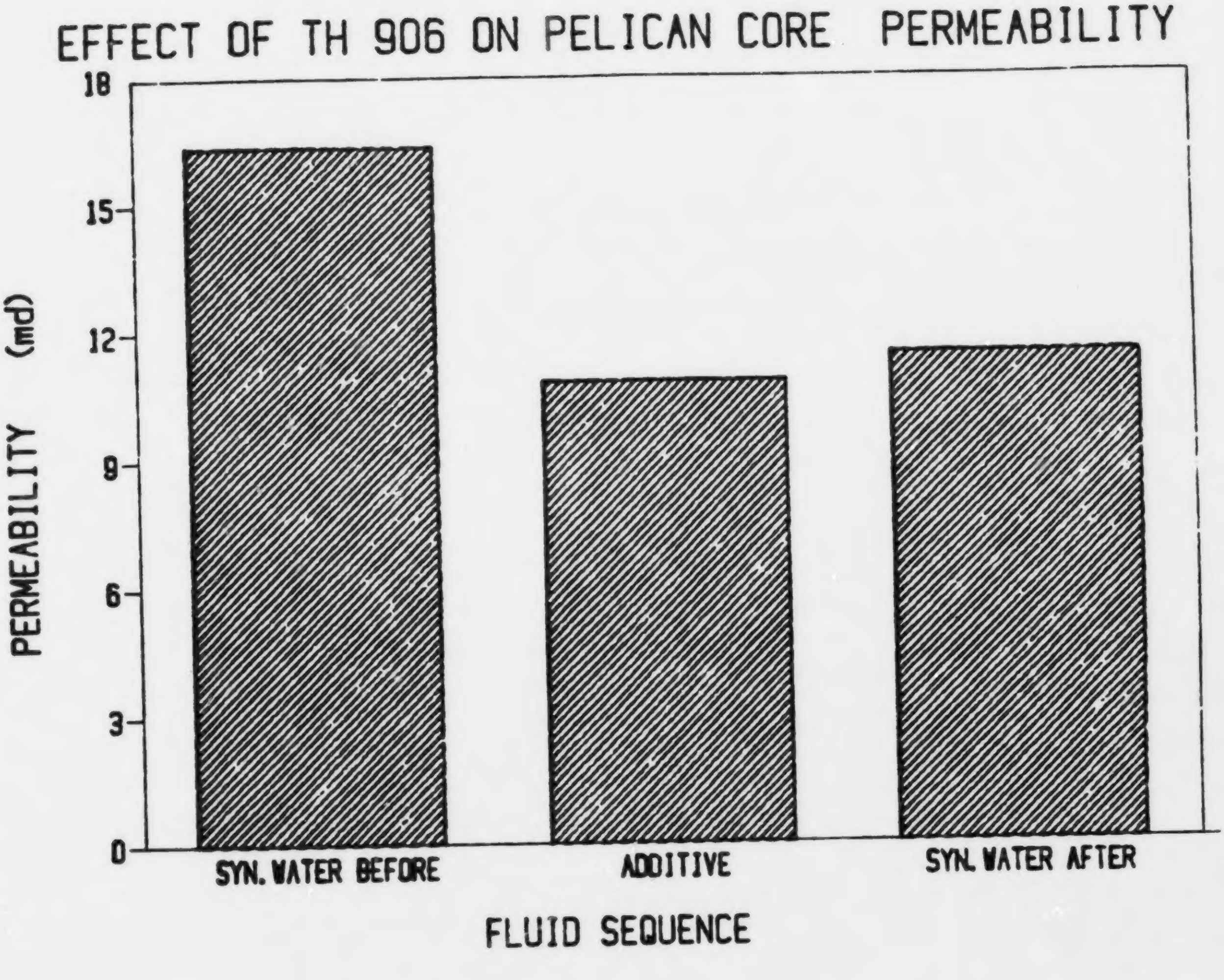

EFFECT OF TH 906 ON PELICAN CORE PERMEABILITY
PERMEABILITY (md)
18
15
12
9
6
3
0
SYN. WATER BEFORE
ADDITIVE
SYN. WATER AFTER
FLUID SEQUENCE

FIGURE 3-6

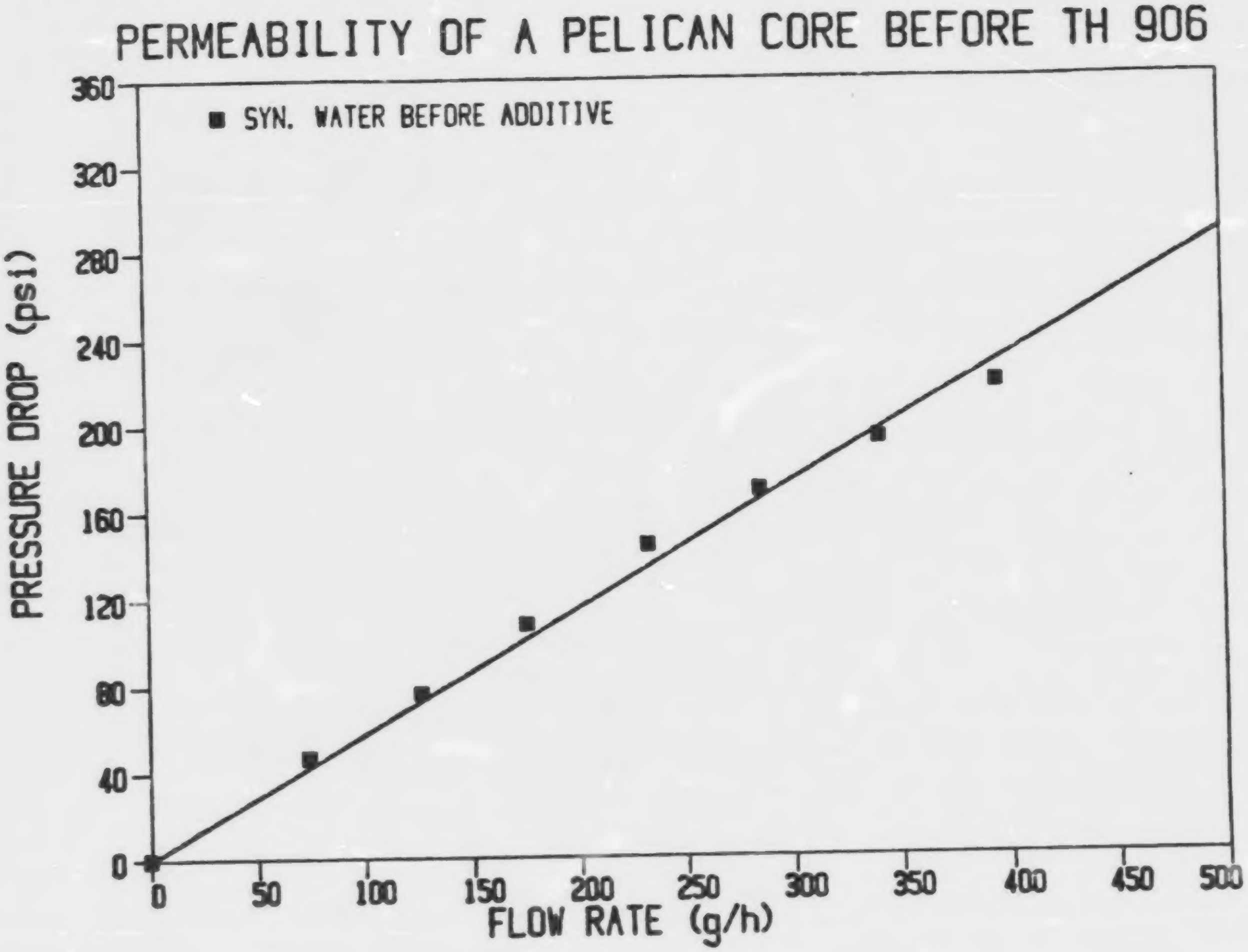

PERMEABILITY OF A PELICAN CORE BEFORE TH 906
■ SYN. WATER BEFORE ADDITIVE
PRESSURE DROP (psi)
360
320
280
240
200
160
120
80
40
0
0
50
100
150
200
250
300
350
400
450
500
FLOW RATE (g/h)

FIGURE 3-7

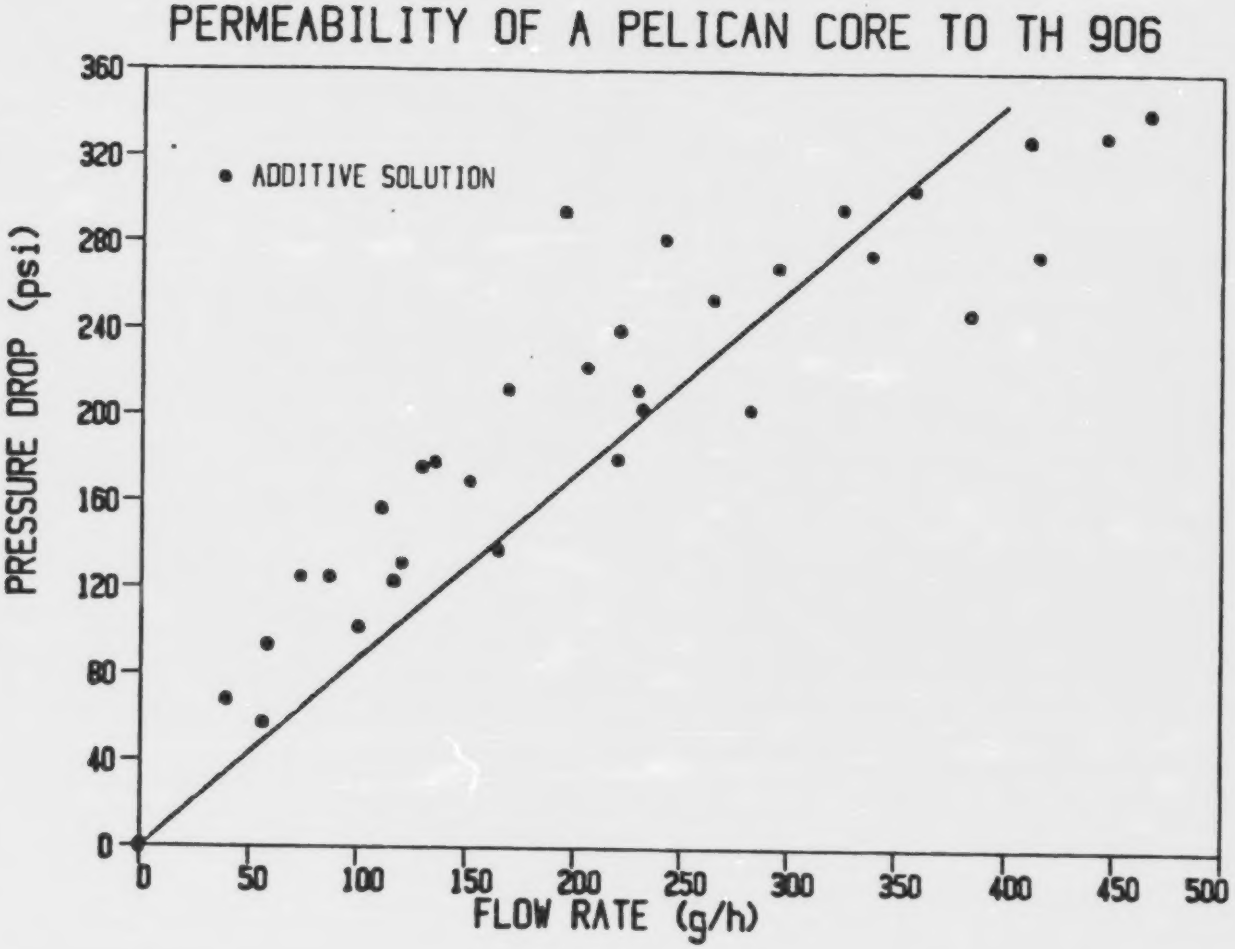

PERMEABILITY OF A PELICAN CORE TO TH 906
● ADDITIVE SOLUTION
PRESSURE DROP (psi)
FLOW RATE (g/h)
0
40
80
120
160
200
240
280
320
360
0
50
100
150
200
250
300
350
400
450
500

FIGURE 3-8

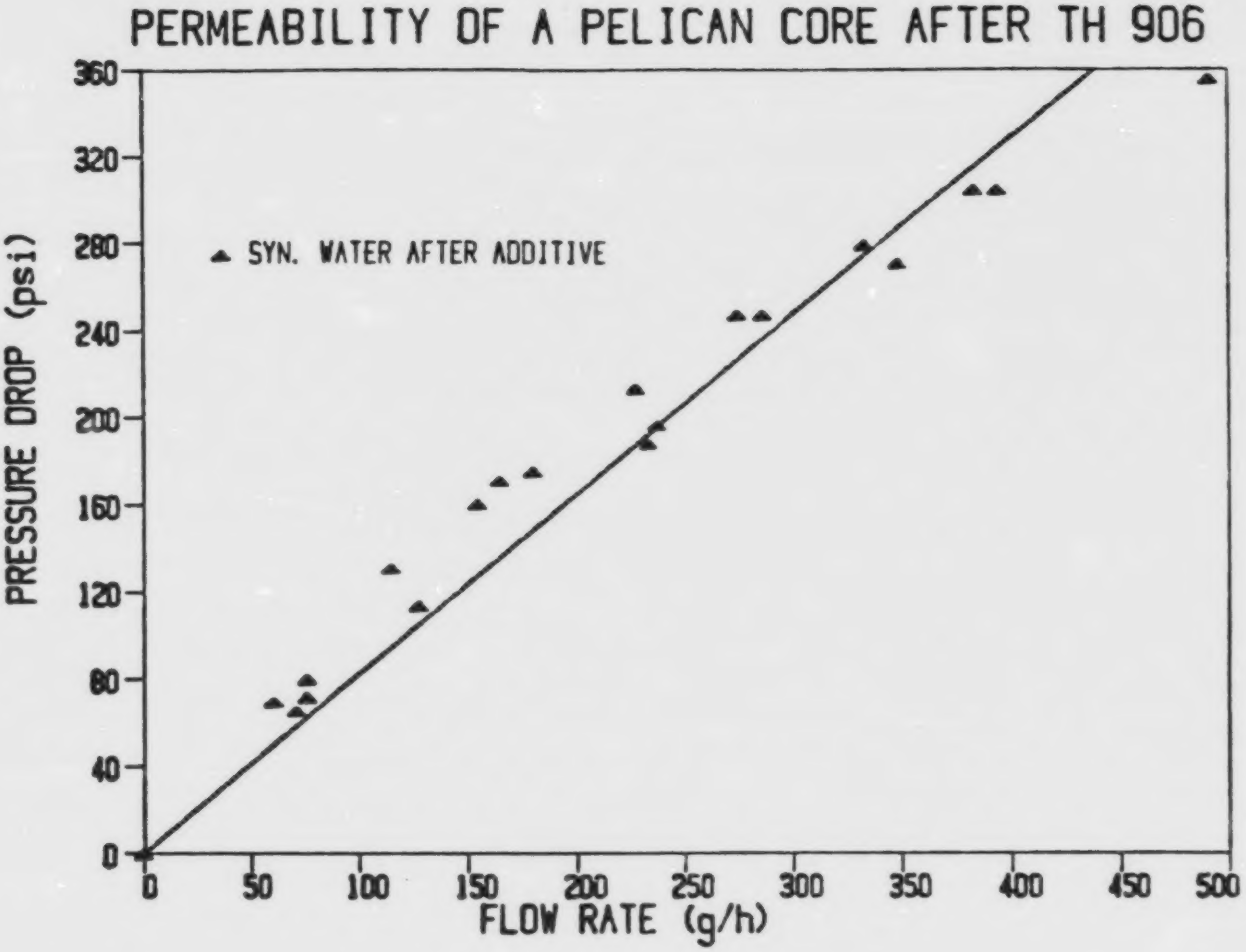

PERMEABILITY OF A PELICAN CORE AFTER TH 906
PRESSURE DROP (psi)
0
40
80
120
160
200
240
280
320
360
FLOW RATE (g/h)
0
50
100
150
200
250
300
350
400
450
500
SYN. WATER AFTER ADDITIVE

FIGURE 3-9

EFFECT OF TRS-410 ON EDAM CORE PERMEABILITY

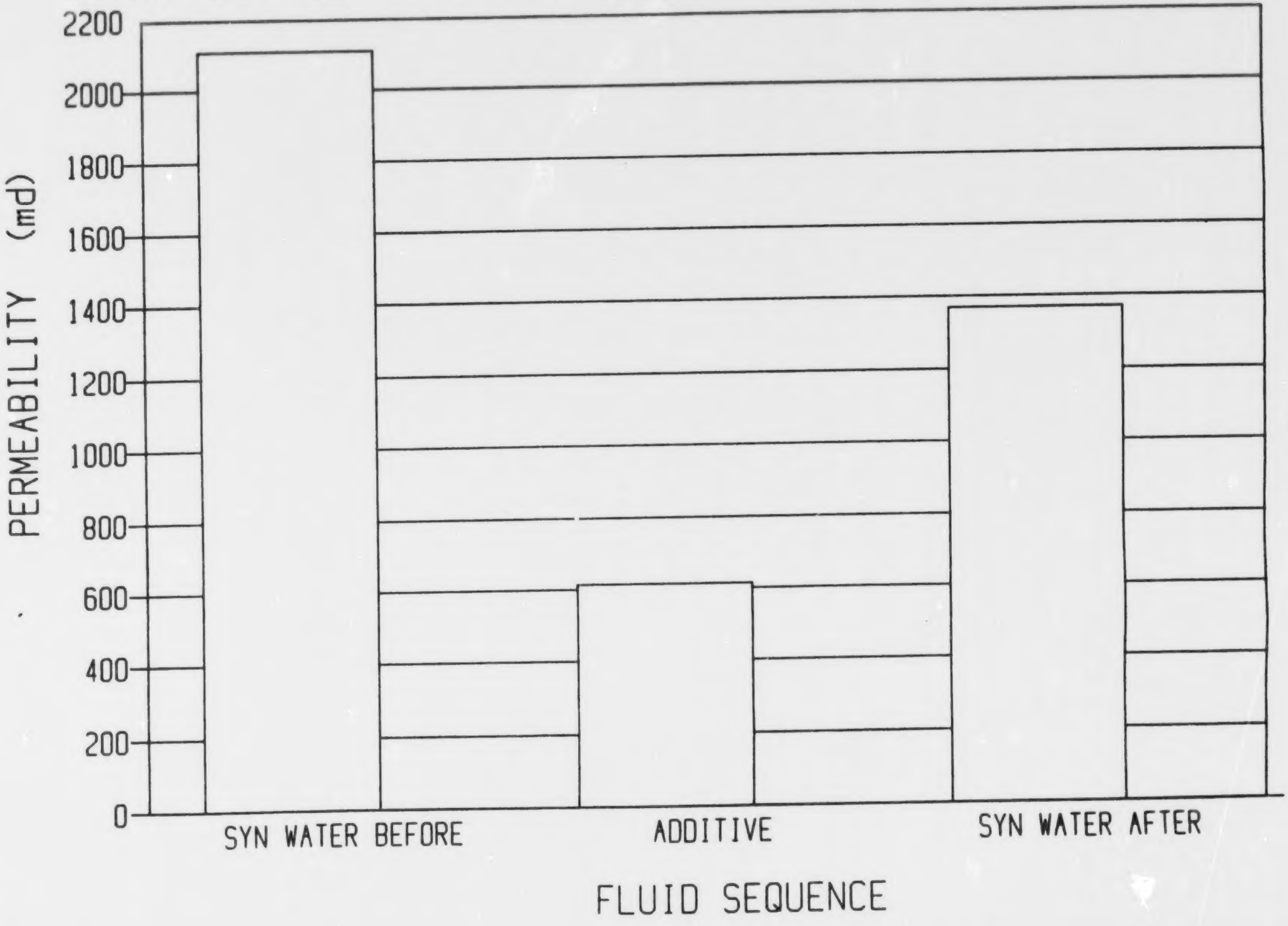


FIGURE 3-10

EFFECT OF TRS 410 ON EDAM CORE PERMEABILITY

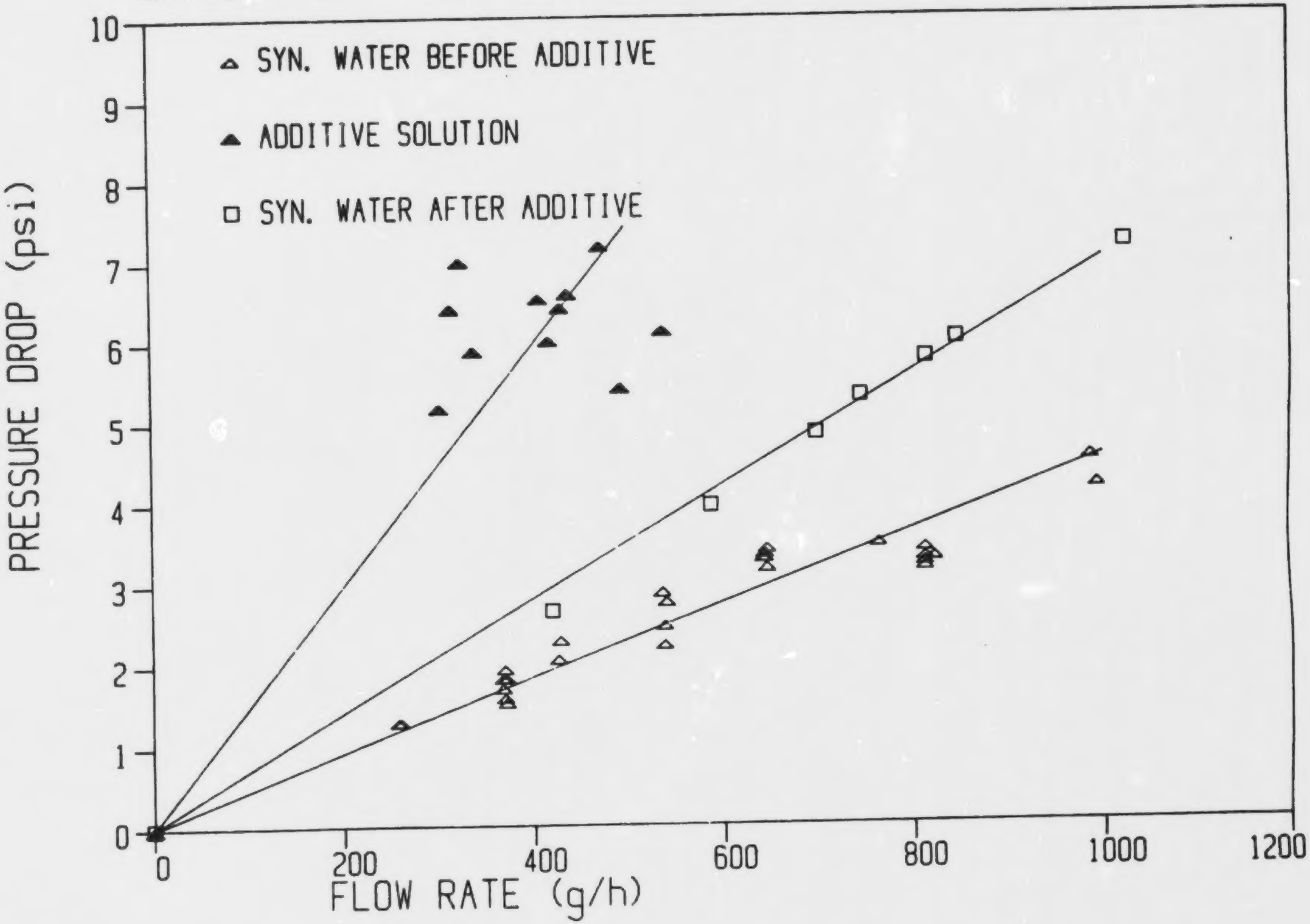


FIGURE 3-11

EFFECT OF TCH-956 ON EDAM CORE PERMEABILITY

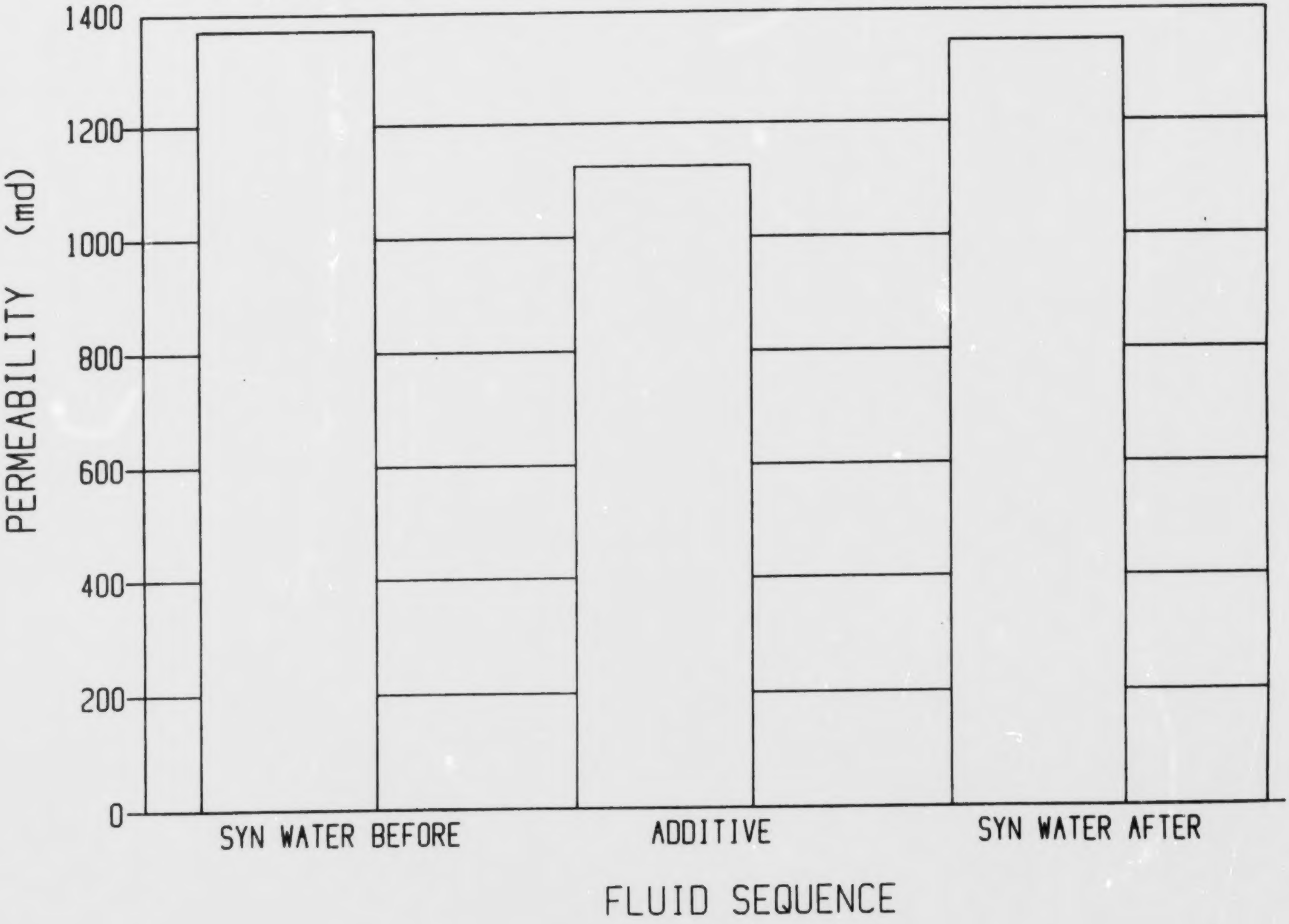


FIGURE 3-12

EFFECT OF TCH 956 ON EDAM CORE PERMEABILITY

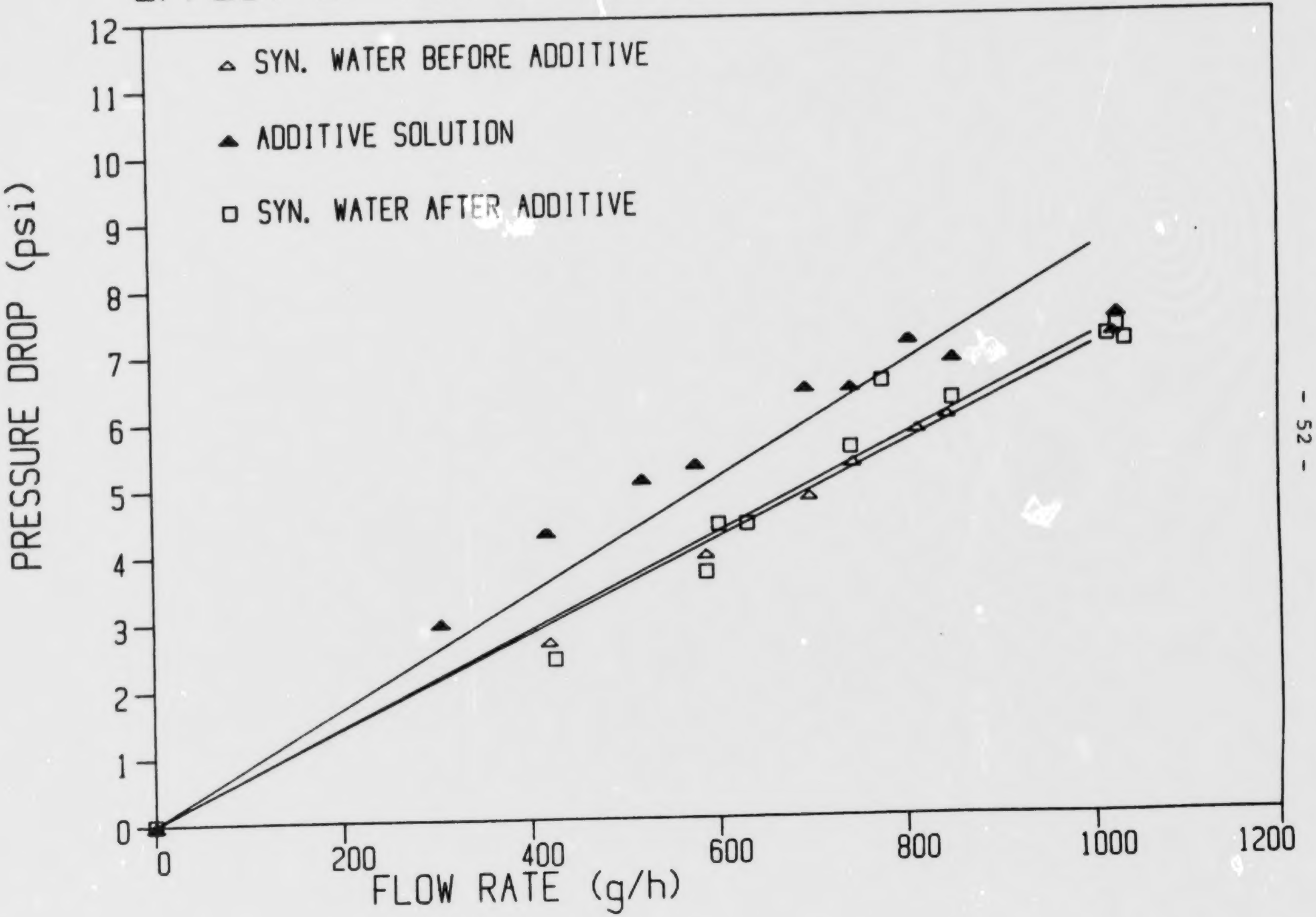


FIGURE 3-13

EFFECT OF THD-906 ON EDAM CORE PERMEABILITY

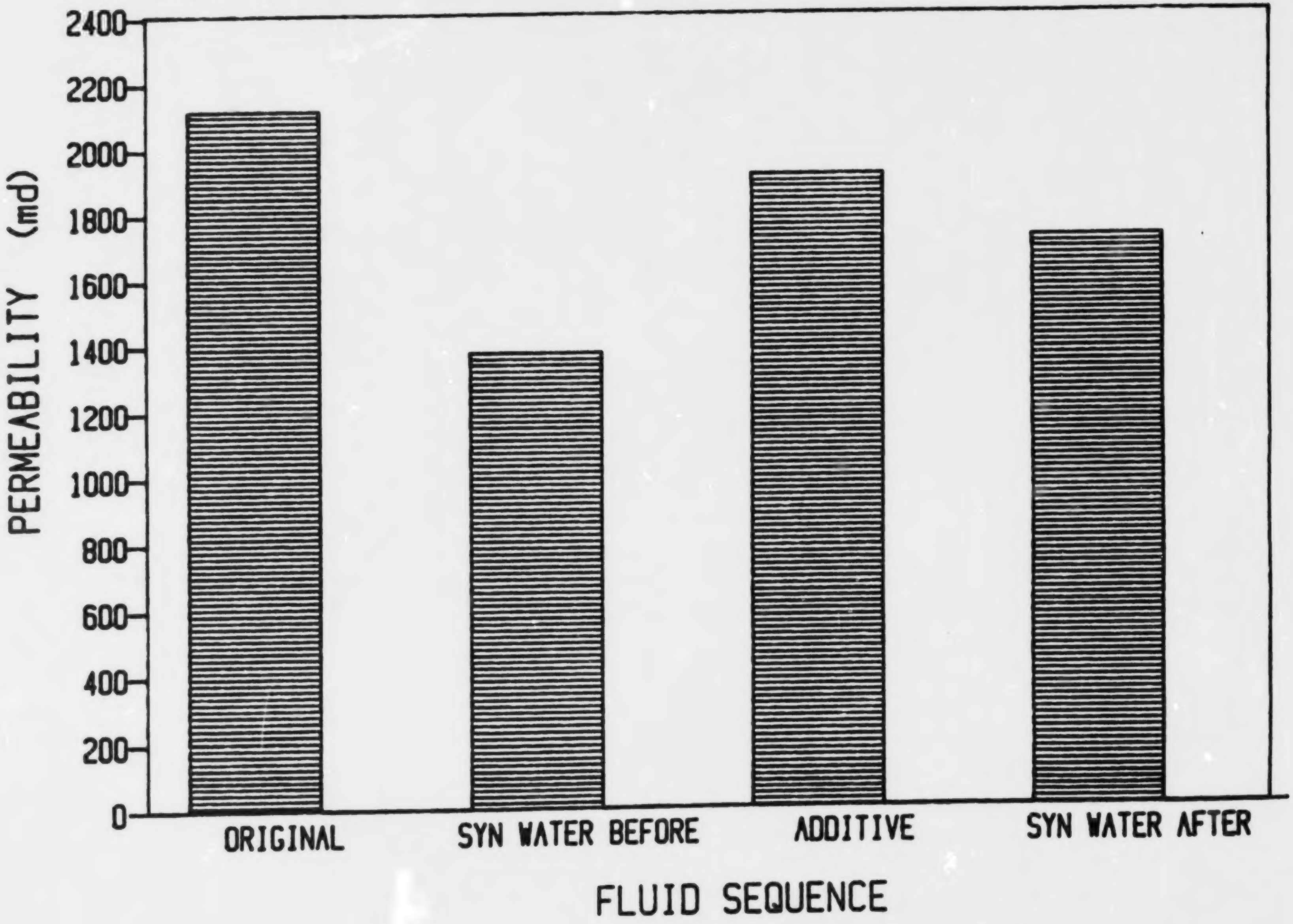
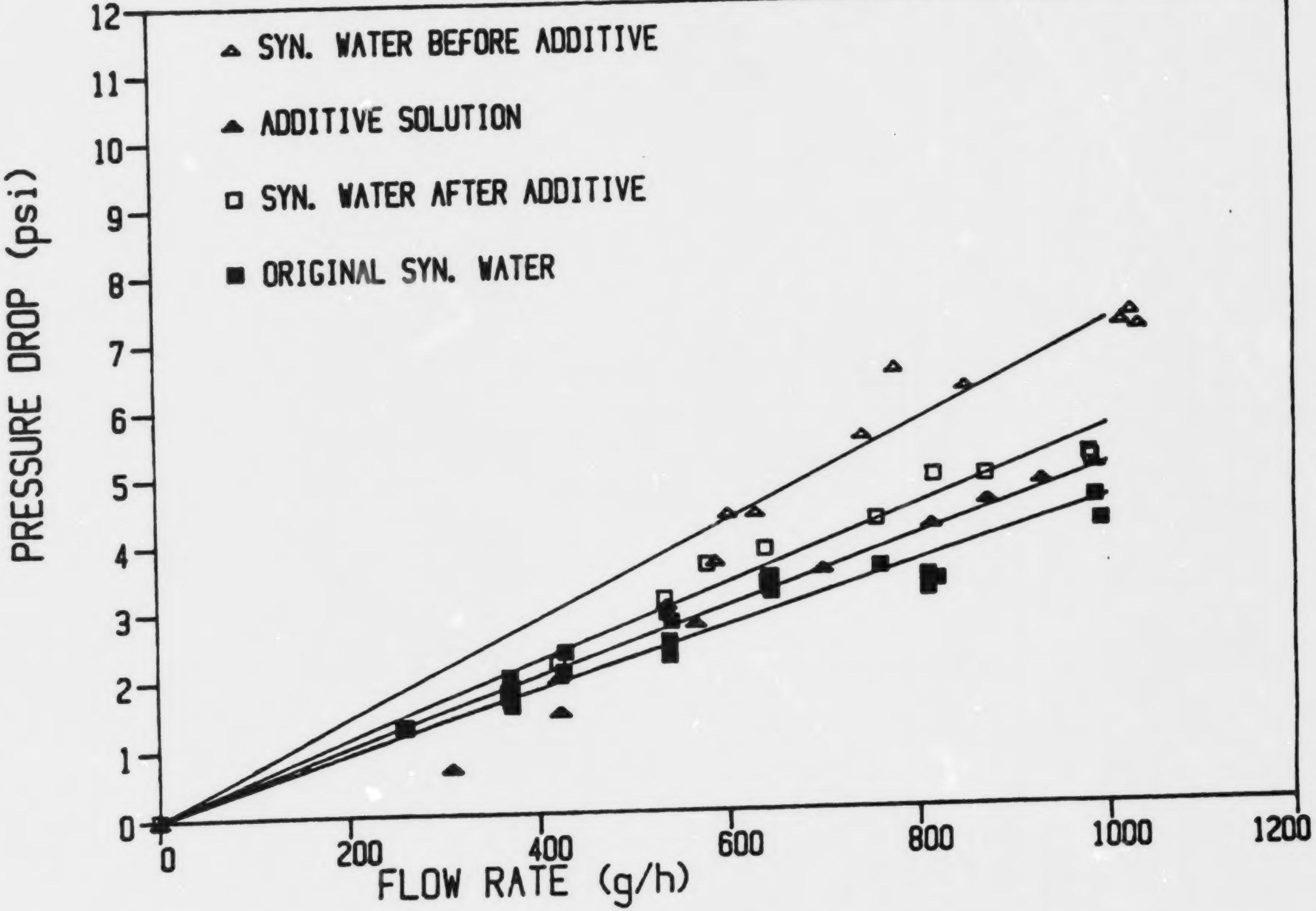


FIGURE 3-14

EFFECT OF TH 906 ON EDAM CORE PERMEABILITY



this limited range of flow rates, non-linearity of pressure drop-flow rate measurements was obvious, in several cases, during additive solution flow. Scatter of the data was also noticeable during the formation water step after additive flow. In such cases, using Darcy's law for permeability estimation represents an approximation.

In all the examined cases a reduction of core permeability, during additive flow, was observed. The permeability varied from about 20% to 70% of the originally measured value. Mixed results were obtained with synthetic formation water after additive solution flow. For the Pelican Lake cores, the permeability continued to show a decline after return to synthetic formation water flow (Figures 3-1, 3-3), except in the case of "Thermoflood 906" experiment. In the latter experiment, some recovery in permeability may be observed in the final formation water flow step, Figure 3-5. A similar trend was also noticeable with the W. Edam core, Figures 3-9 and 3-11.

Scatter of the flow rate - pressure drop data points was particularly pronounced in the case of the petroleum sulfonate additive TRS-410. This may be attributed to strong interactions with the core material, and possibly to foaming effects.

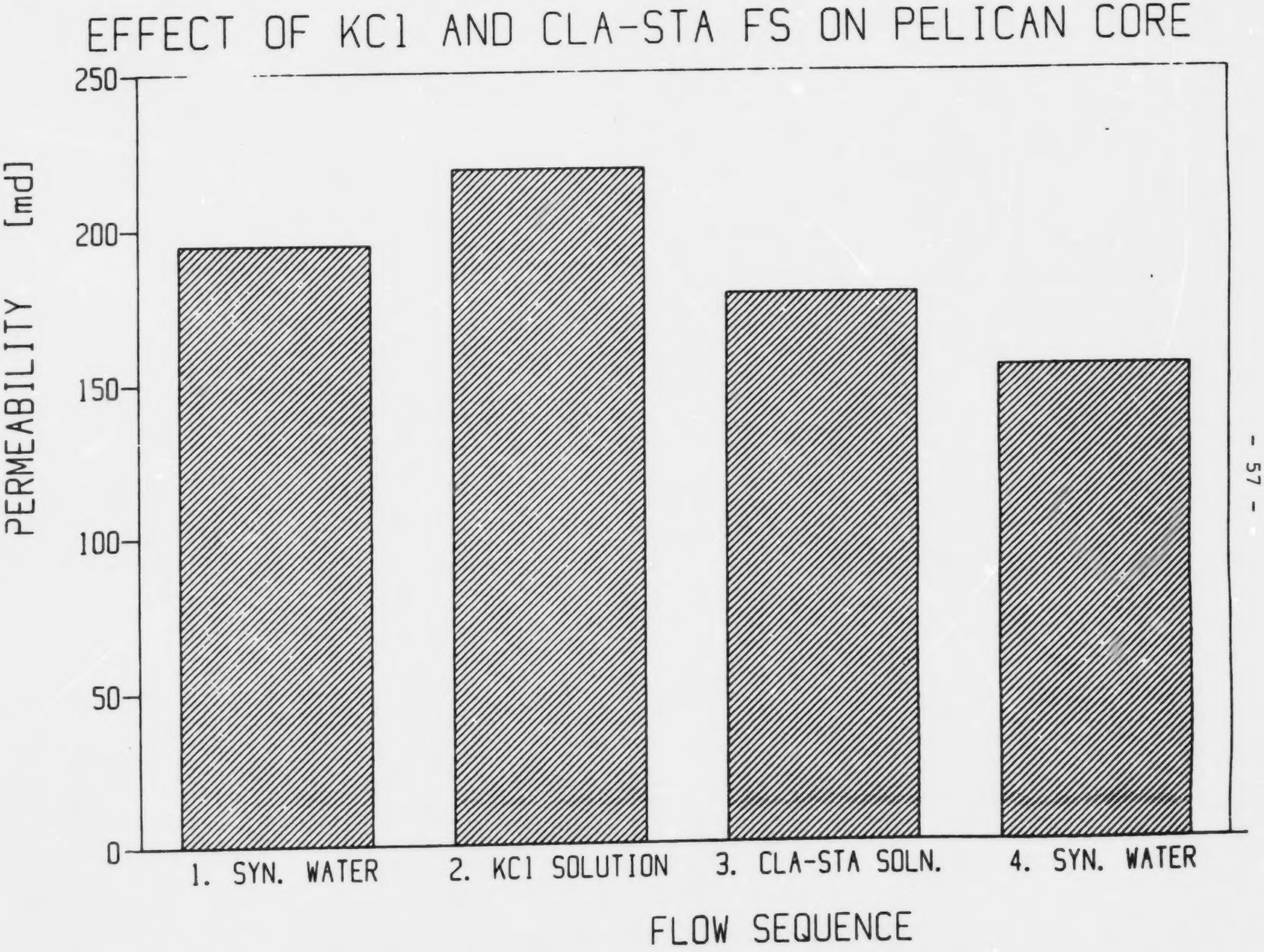
For the W. Edam core sample (Figures 3-9, 3-11 and 3-13) show the actual sequence of fluids used in the experiment. As shown in this series of figures, this flow sequence was synthetic formation water, TRS-410 solution, synthetic formation water, TCH-956 solution, synthetic formation water, Thermoflood 906, and finally synthetic formation water. It is clear that, in spite of using one preserved core for all additive solutions, the general trends observed with the Pelican cores persisted. The sulfonate additive "TRS 410" showed the strongest interactions, while "Thermoflood 906" had the most favourable permeability effects. In the case of the W. Edam core, some recovery of permeability was obtained by flushing and flowing of synthetic formation water.

3.3 Effect of Clay Stabilizers on Permeability

Figures 3-15 to 3-20 show the results of testing the three clay stabilizers (CLA-STA FS, Thermoflo 106, and KOH) with three fresh Pelican Lake core samples. Figures 3-21 to 3-26, show the corresponding results for three different W. Edam core samples. Like the steam interfacial additive experiments, a fixed flow sequence was adopted to evaluate the core permeability before, during and after additive flow. After the initial synthetic formation water flow, an additional flow step, using 4 wt% KCl solution, was introduced before the clay stabilizer flow step in a number of experiments (Figures 3-15, 3-17, 3-21). Potassium chloride is a well known temporary clay stabilizer, which has been used in field applications for many years. It was felt that it would be instructive to compare its effect with the additives being examined in this study. It is useful to observe that in each of the three cases where KCl was introduced, a slight permeability improvement, during KCl solution flow, was achieved. This may be attributed to a favourable ionic exchange with the clay particles.

The additive flow, on the other hand, has consistently resulted in permeability reduction. This reduction, however, varied from one additive to another. Different types of cores (W. Edam vs. Pelican) showed also varied permeability response to the different additives.

FIGURE 3-15



EFFECT OF KCl AND CLA-STA FS ON PELICAN CORE

FIGURE 3-15

EFFECT OF CLA-STA FS ON PELICAN CORE PERMEABILITY

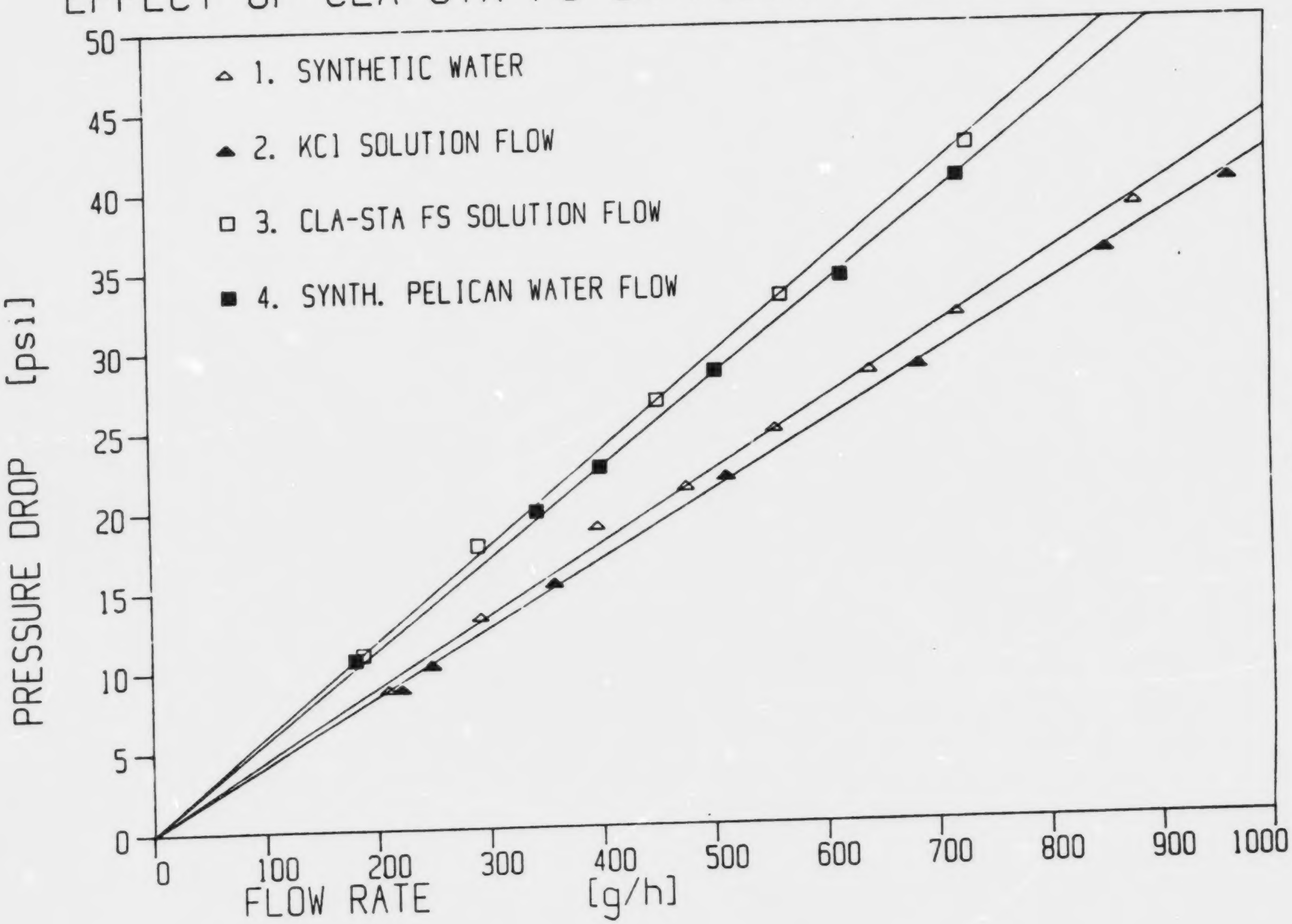


FIGURE 3-17

EFFECT OF THF-106W ON PELICAN CORE PERMEABILITY

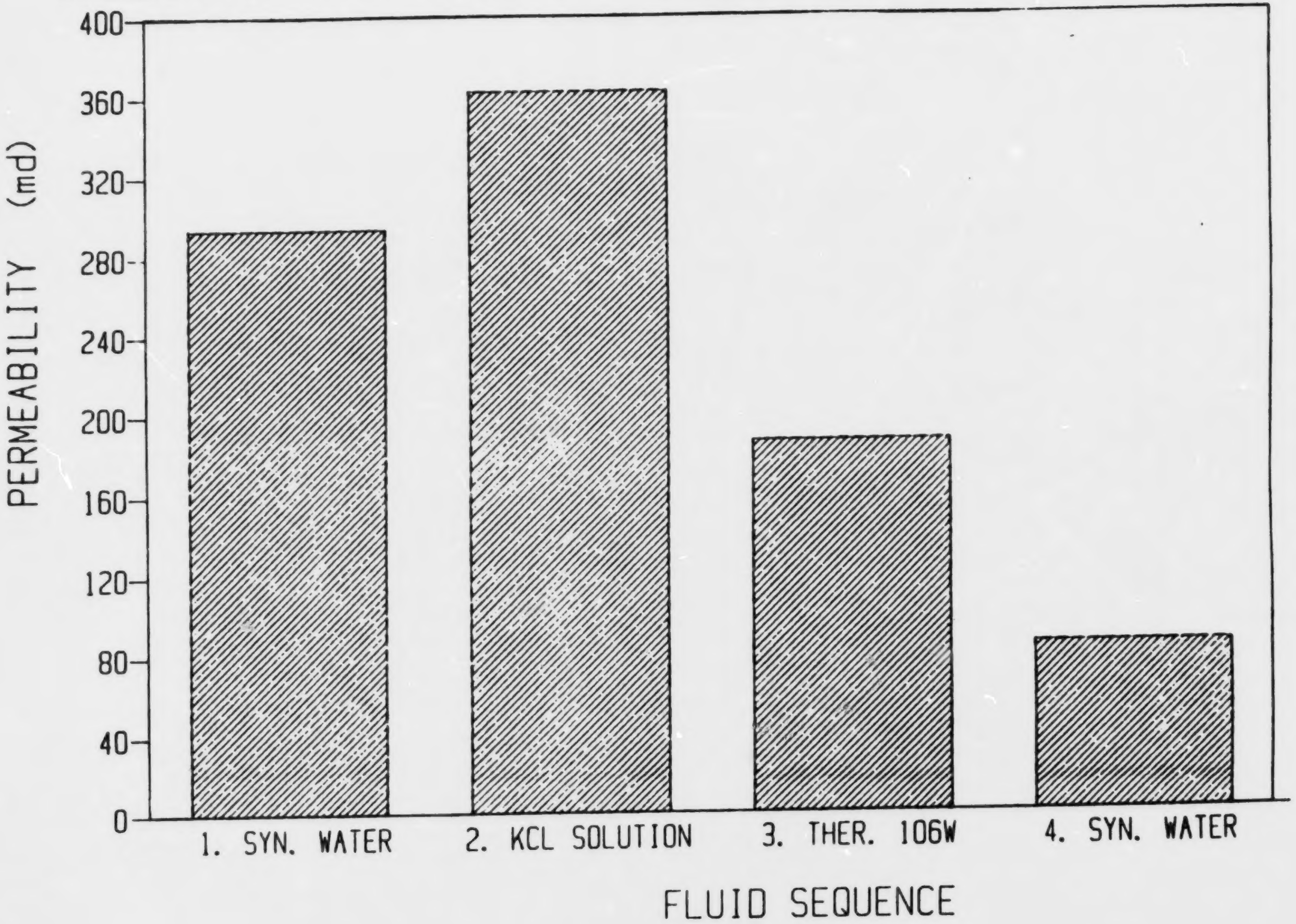


FIGURE 3-18

EFFECT OF THF-106W ON PELICAN CORE PERMEABILITY

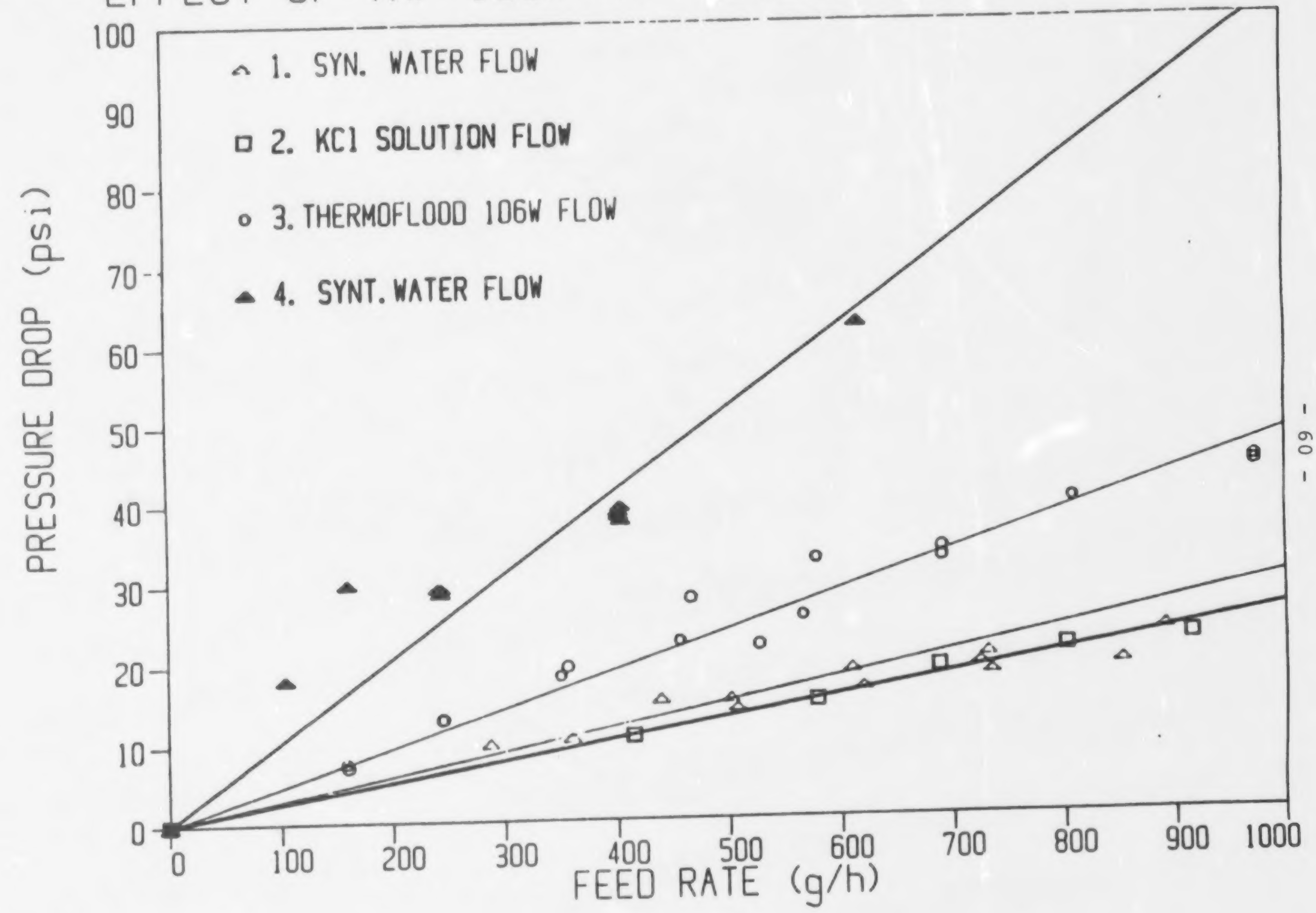


FIGURE 3-19

EFFECT OF KOH SOLN ON PELICAN CORE PERMEABILITY

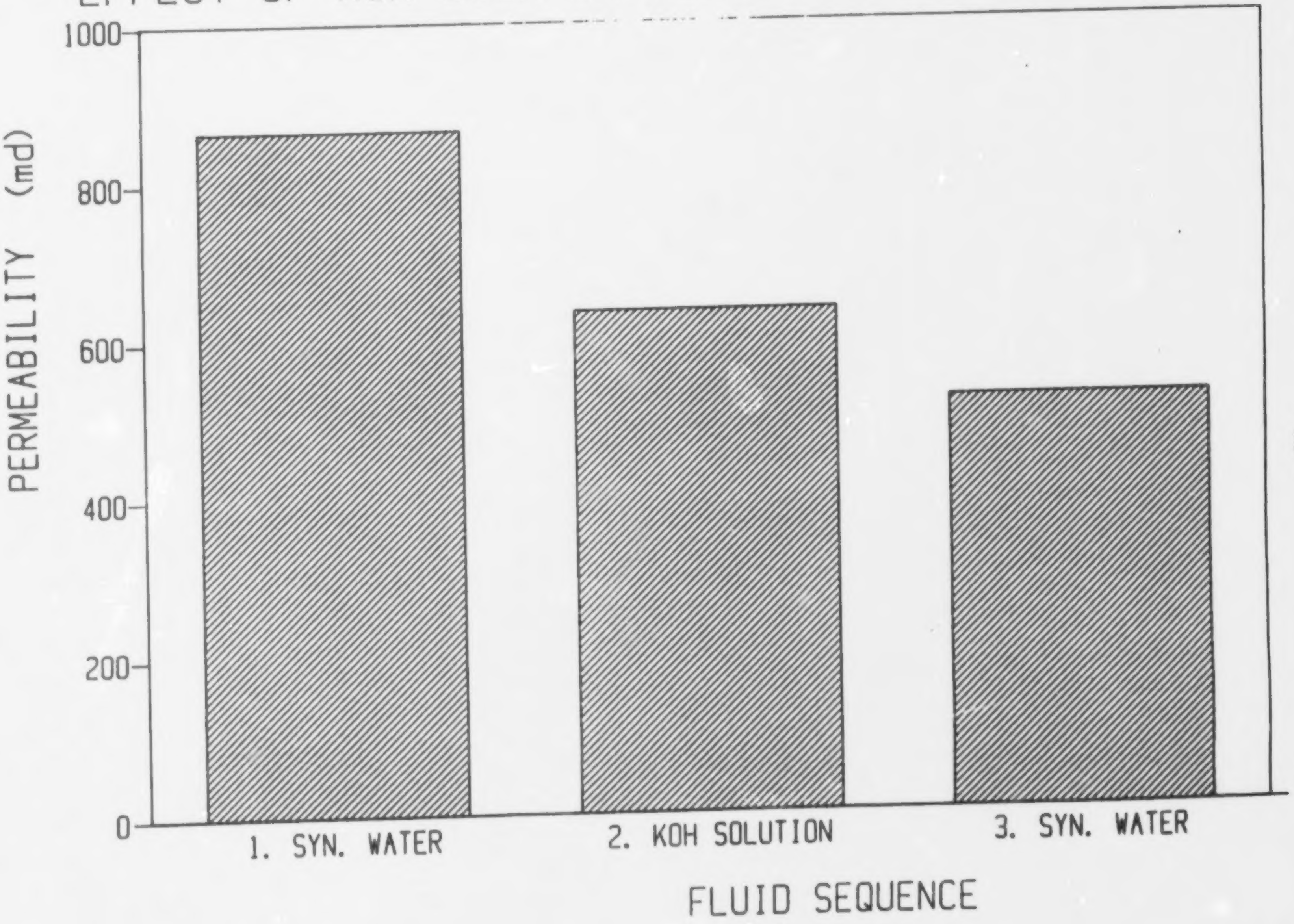


FIGURE 3-20

EFFECT OF KOH SOLN ON PELICAN CORE PERMEABILITY

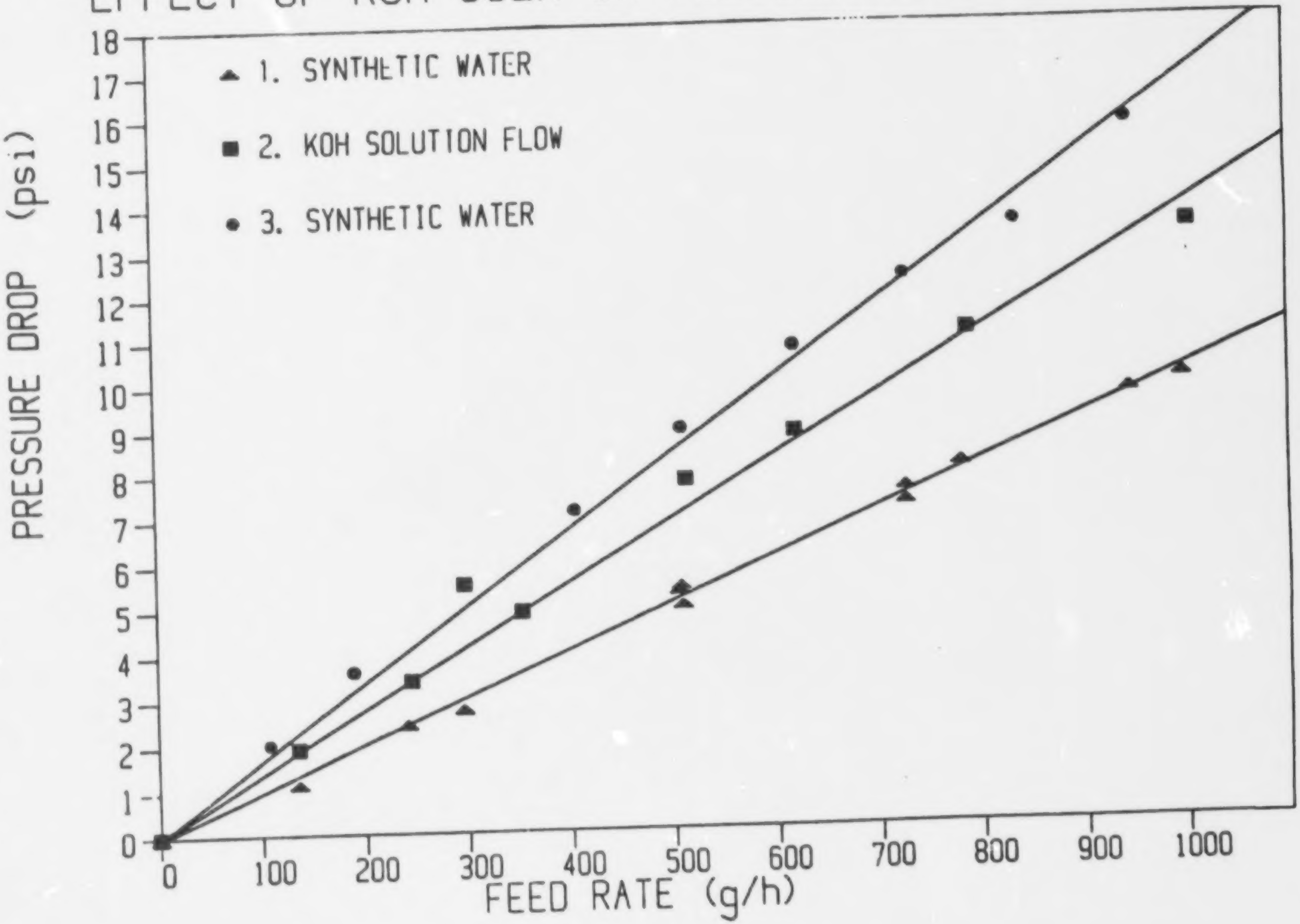


FIGURE 3-21

EFFECT OF CLA STA FS ON W. EDAM CORE PERMEABILITY

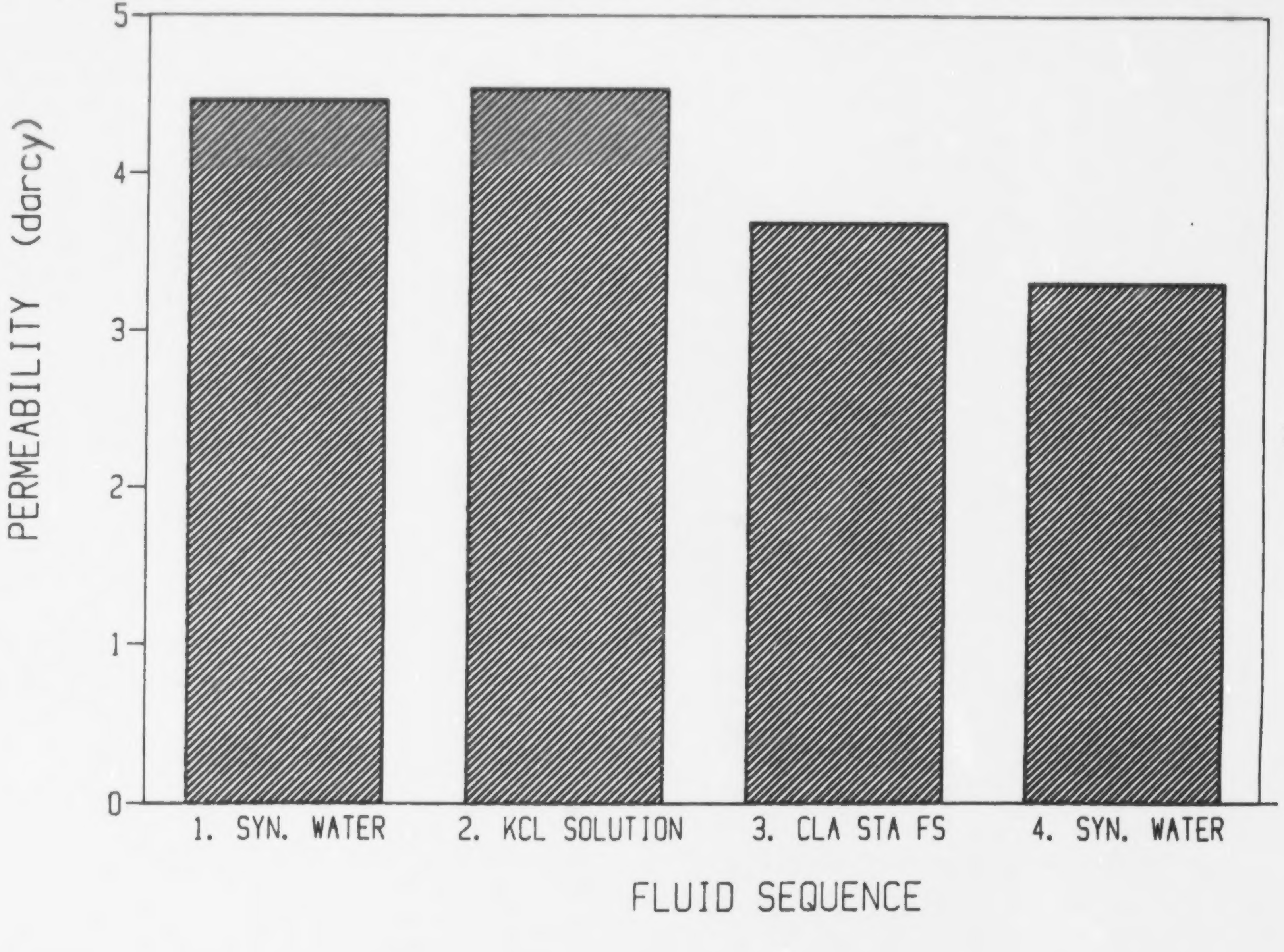


FIGURE 3-22

EFFECT OF CLA STA FS ON W. EDAM CORE PERMEABILITY

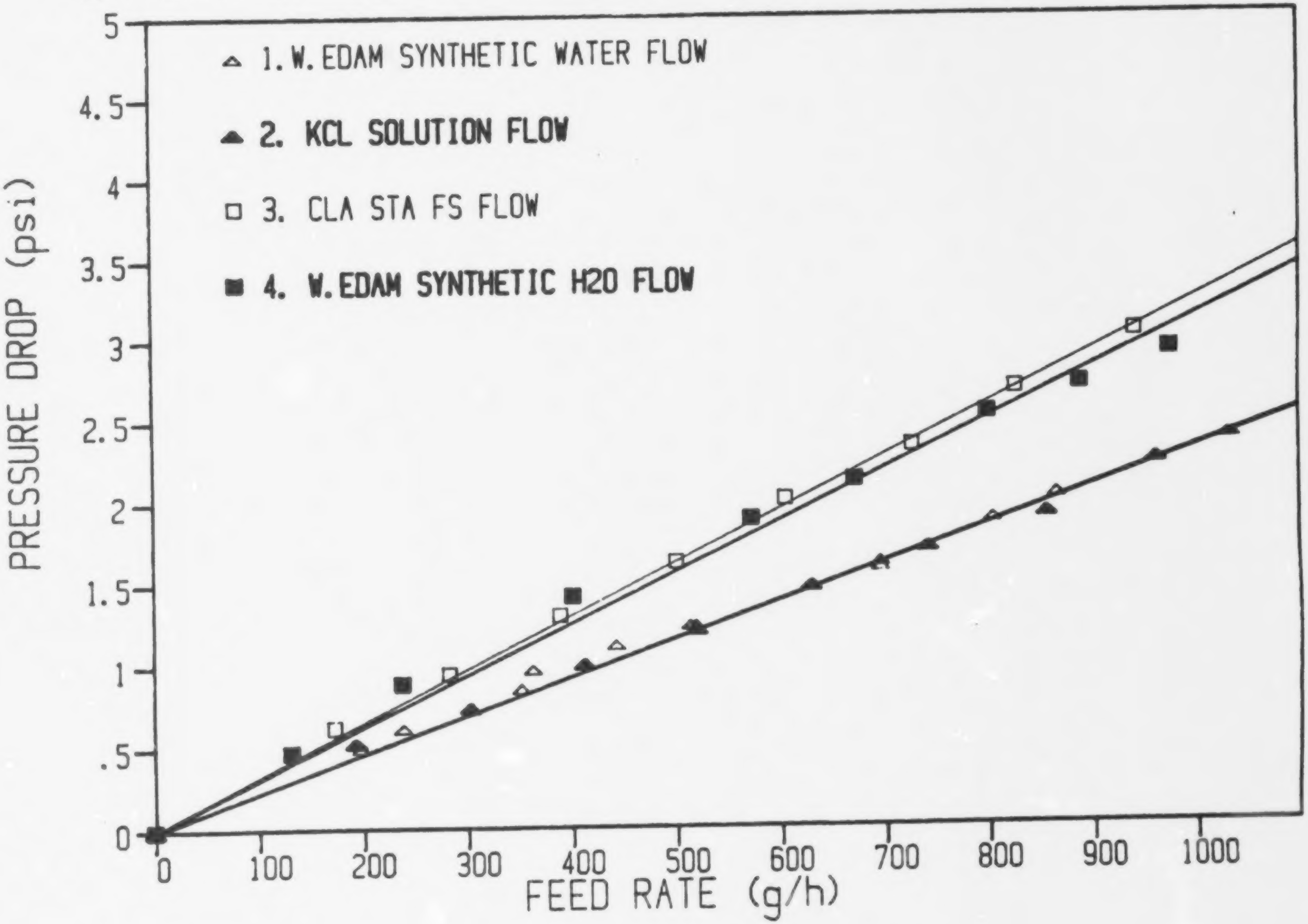


FIGURE 3-23

EFFECT OF THF 106W ON W.EDAM CORE PERMEABILITY

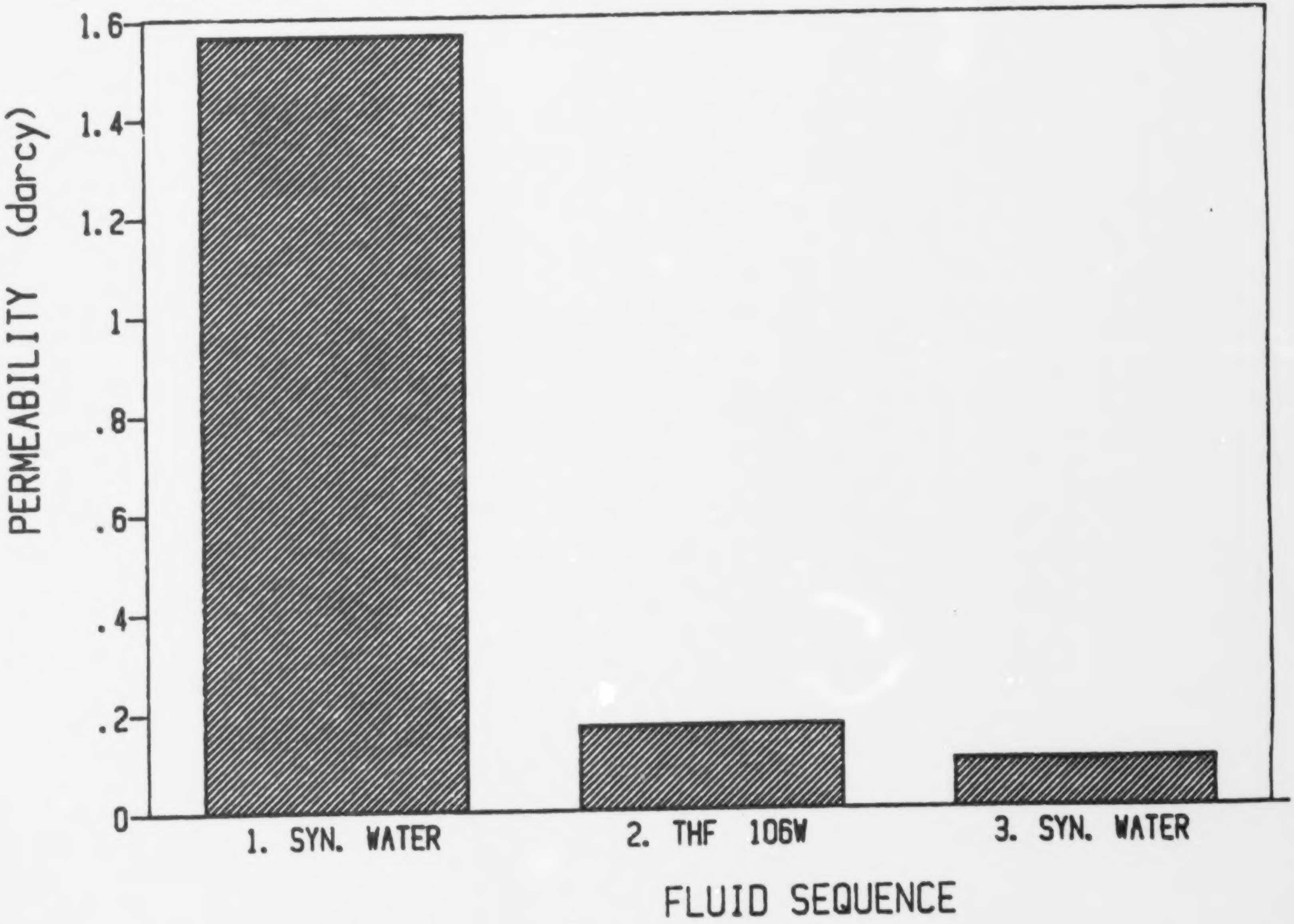


FIGURE 3-24

EFFECT OF THF 106W ON W. EDAM CORE PERMEABILITY

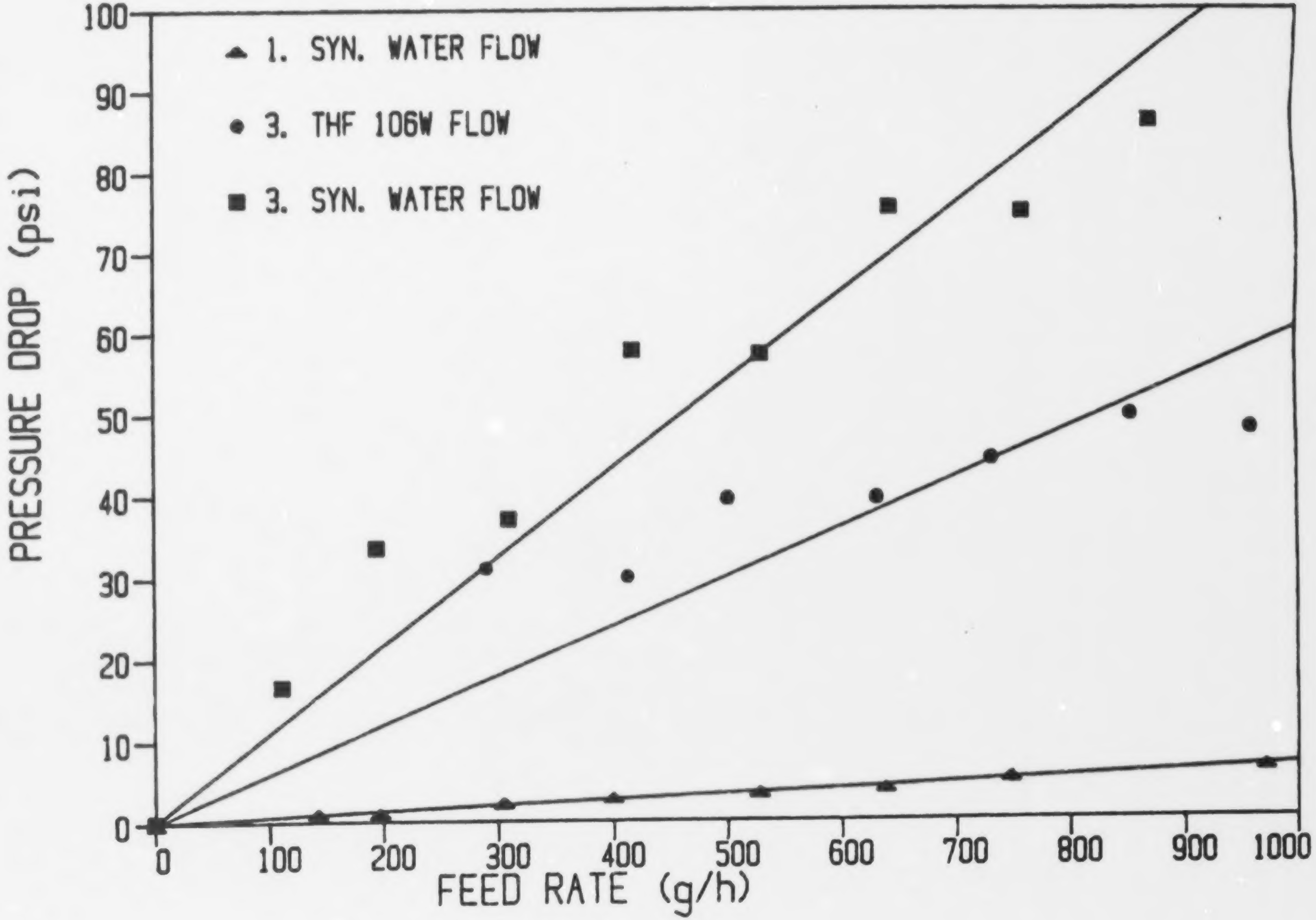
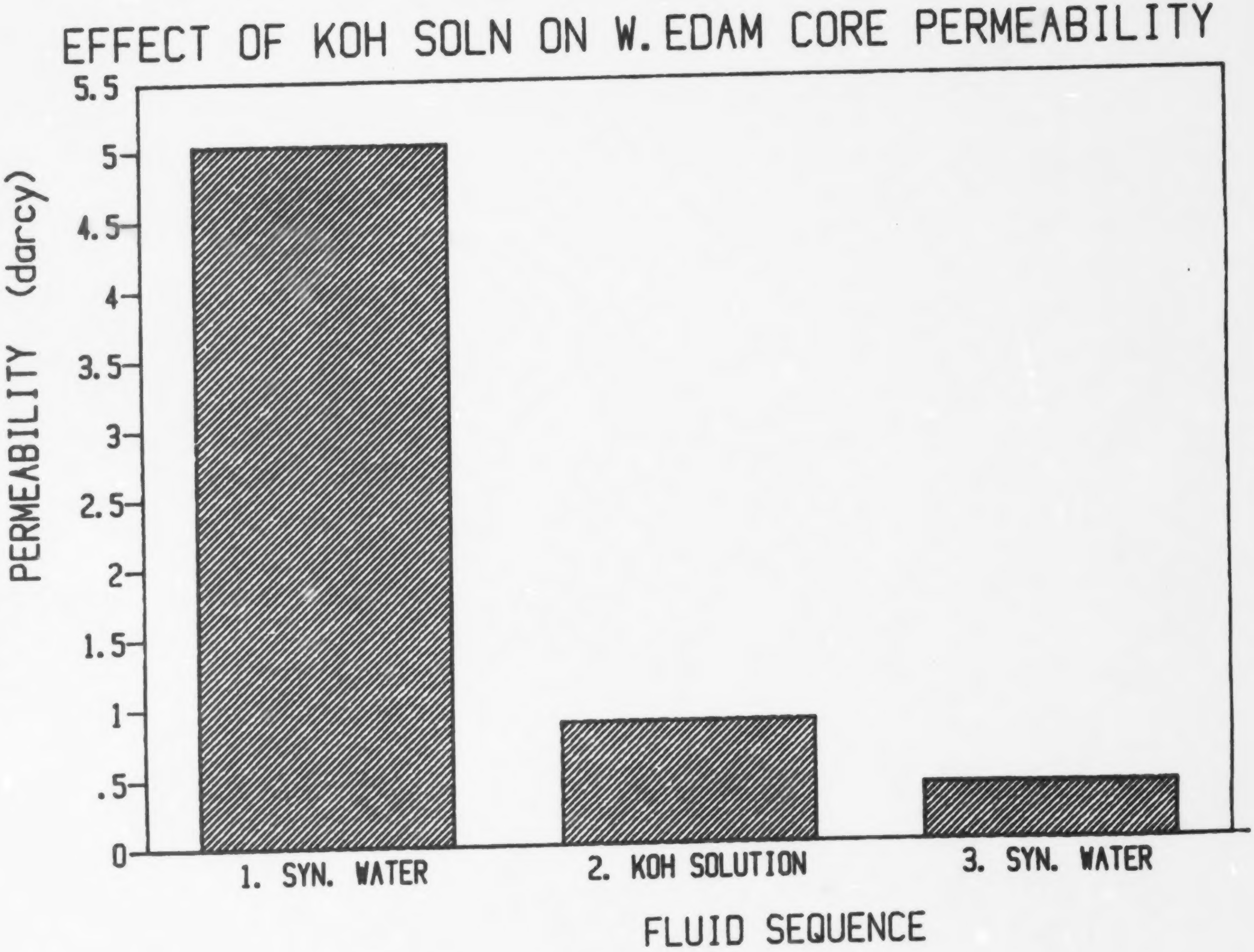


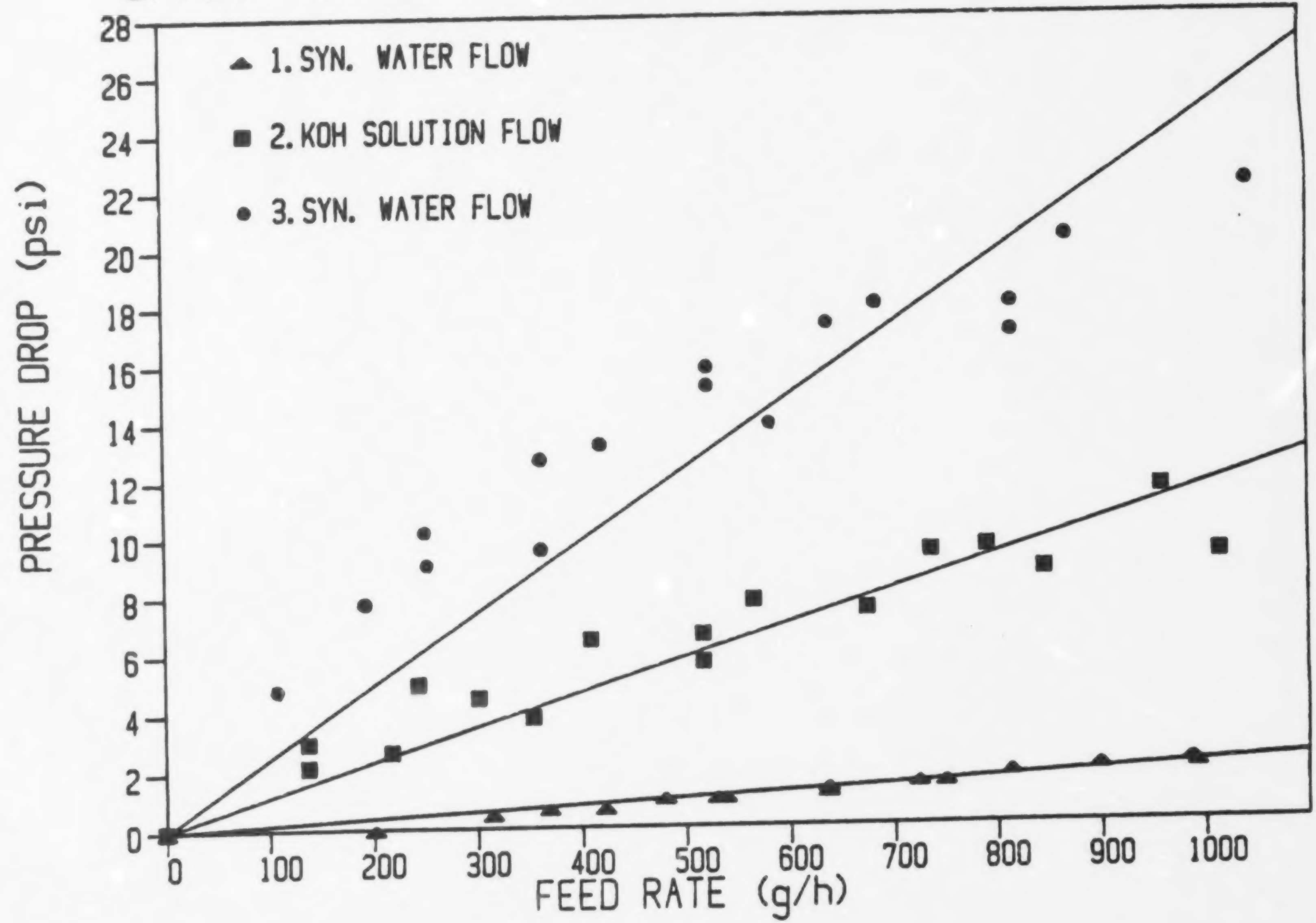
FIGURE 3-25



EFFECT OF KOH SOLN ON W. EDAM CORE PERMEABILITY

FIGURE 3-26

EFFECT OF KOH SOLN ON W. EDAM CORE PERMEABLITY



The most favourable interactions were those of CLA-STA FS, with both the W. Edam and Pelican core samples. Thermoflo 106W, on the other hand, showed very unfavourable interactions, particularly with the W. Edam core sample. Nearly an order of magnitude reduction in permeability was observed in the latter case.

4. EFFECT OF ADDITIVES ON OIL DISPLACEMENT

Comparative displacement experiments, with and without additives, have been conducted to test the relative effect of the three interfacially active agents (Thermoflood 906, TCH-956 and TRS-410) on oil recovery. The results of the experiments are supported by appropriate statistical analysis to test the significance of the data. All the experiments have been carried out using homogeneous sand columns, applying a standardized packing procedure. The use of synthetic sand cores was decided to minimize the effects of such complicating factors as large variability in pore size distribution, permeability and wettability; thus, enabling meaningful comparison of the results.

Few additional displacement experiments involving each of the clay stabilizers (CLA-STA FS, Thermoflo 106W, and KOH) together with one of the steam additives have also been carried out. Synthetic cores similar to those used with the steam additives have been used. In these cores, however, a certain constant percentage (5%) of selected clays was homogeneously mixed with the Ottawa sand in the packed columns.

4.1 Oil Displacement Experiments

In all the displacement experiments, the sand packs were saturated with either W. Edam or Pelican Lake heavy oil, depending on the condition of the run, with a brine solution at the irreducible connate level. The synthetic cores contained well mixed Ottawa sand, ASS #35, packed in 28 in. long, 1 in. O.D., 316 SS (ASTM D-213) tubing. Several identical core holders were used. A sand core was prepared by consistently packing a preweighed amount of sand (495 ± 3 g), from a homogeneous mixture, employing a standardized dry packing technique. The average porosity and permeability of these synthetic cores were

0.35 and 44 darcy, respectively. The injection fluid feed rate was 200 g/h in all the runs; and a back pressure of 500 psig was maintained at the system collection point in every case. The displacement experiments were carried out at temperatures of 100, 200 and 250°C. The displaced product was collected at five minute intervals at the beginning of each run, and at longer intervals later in the run. The entire product, collected at the end of each time interval, was analyzed for water/oil content.

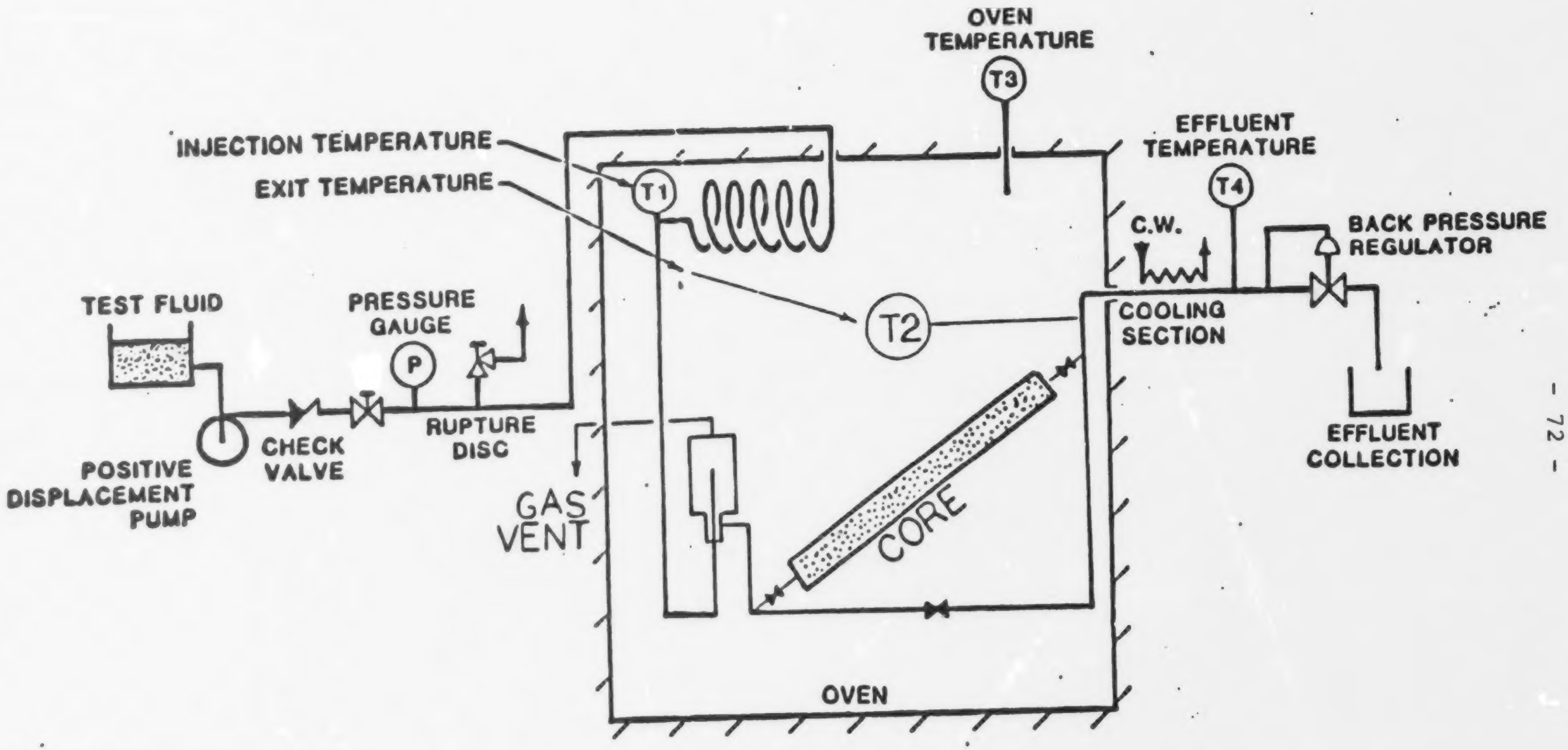
Excluding the specifics of each run (i.e. additive type, operating temperature, and oil used), all the displacement experiments followed the same general procedure. This procedure is outlined in the following:-

- The sand core was saturated with brine solution at room temperature.

- Several pore volumes of oil, heated to about 65°C to facilitate injection, were continuously fed to displace the water in the core. Oil injection was continued until the ater saturation was reduced to the connate level (determined to be approximately 6%).

- The core section was isolated, using the inlet and outlet valves shown in Figure 4-1. The core was then by-passed and the oil in the inlet and outlet pipework was flushed with solvent. Flushing continued until all connecting pipework was clean and free of oil. With the core still isolated, the solvent in the connecting inlet, outlet, and by-pass piping was completely displaced with brine. The process of cleaning the inlet and outlet piping, to the core, was necessary for accurate monitoring of the oil displacement, and facilitated a convenient calculation of oil recovery as a function of fluid injection.

FIGURE 4-1


OVEN TEMPERATURE
T3
INJECTION TEMPERATURE
EXIT TEMPERATURE
T1
EFFLUENT TEMPERATURE
T4
C.W.
BACK PRESSURE REGULATOR
TEST FLUID
PRESSURE GAUGE
P
T2
COOLING SECTION
CHECK VALVE
RUPTURE DISC
EFFLUENT COLLECTION
POSITIVE DISPLACEMENT PUMP
GAS VENT
CORE
OVEN

SYNTHETIC CORE DISPLACEMENT SET-UP

- The core inlet and outlet valves were then opened, the core by-pass was closed, and fluid injection was started at the pre-specified constant rate, and at the pre-set temperature.
- The injection fluid (water or additive solution) was pumped through 40 feet of 1/4 in. coil before it reached the core. The coil was kept in a constant temperature oven maintained at 100, 200 or 250°C temperature, depending on the conditions of the run. The oven temperature, hot water injection temperature, and core exit temperature were monitored throughout each run. They remained quite uniform close to the oven set temperature, in all the experiments.
- The displaced product was collected, as earlier indicated, and analyzed using the standard Dean-Stark method.
- The run was terminated after injection up to 10 pore volumes of fluid.

4.2 Oil Displacement Results

The complete sets of Pelican oil displacement results are given in Figures 4-2 to 4-7, for three different temperatures (100, 200 and 250°C). The figures compare the performance of the additives with water, as shown by their effect on oil recovery and water-oil ratios, at each of the three fixed temperatures, 100, 200 and 250°C. Similar sets of results for the W. edam oil are given in Figures 4-8 to 4-13.

FIGURE 4-2

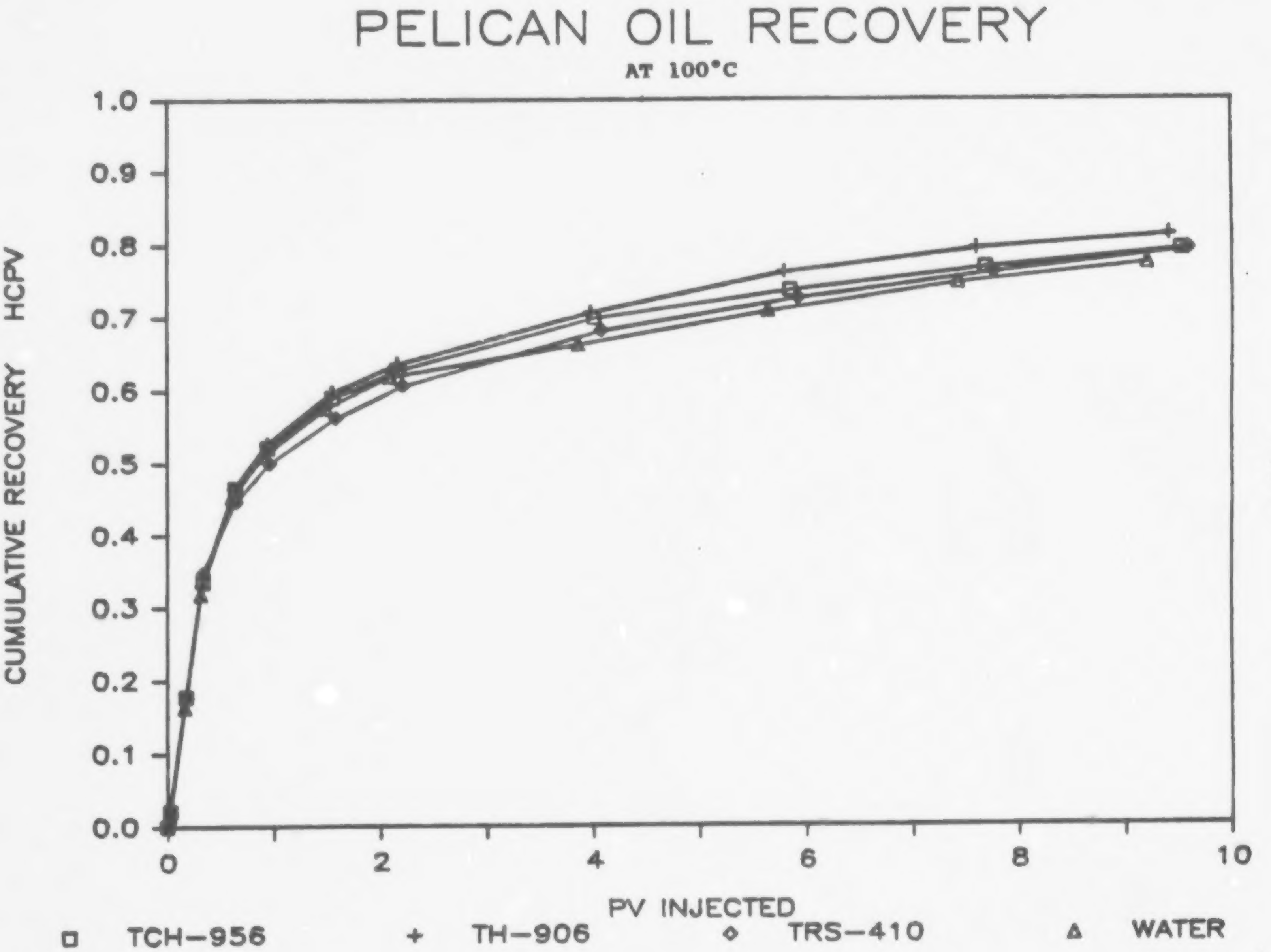

PELICAN OIL RECOVERY
AT 100°C
CUMULATIVE RECOVERY HCPV
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
PV INJECTED
□ TCH-956
+ TH-906
◇ TRS-410
△ WATER

FIGURE 4-3

PELICAN WATER—OIL RATIO

AT 100°C

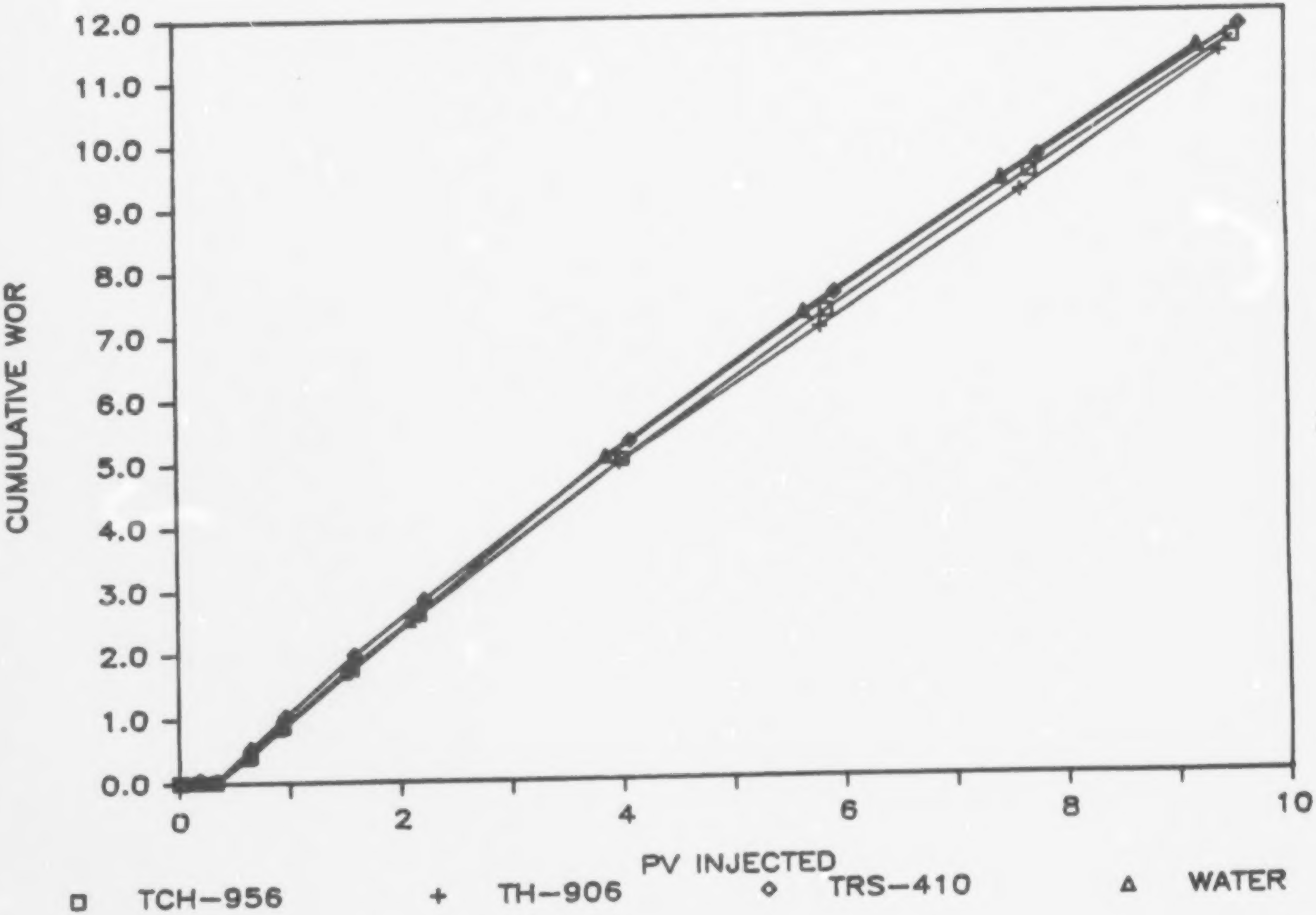


FIGURE 4-4

PELICAN OIL RECOVERY

AT 200C

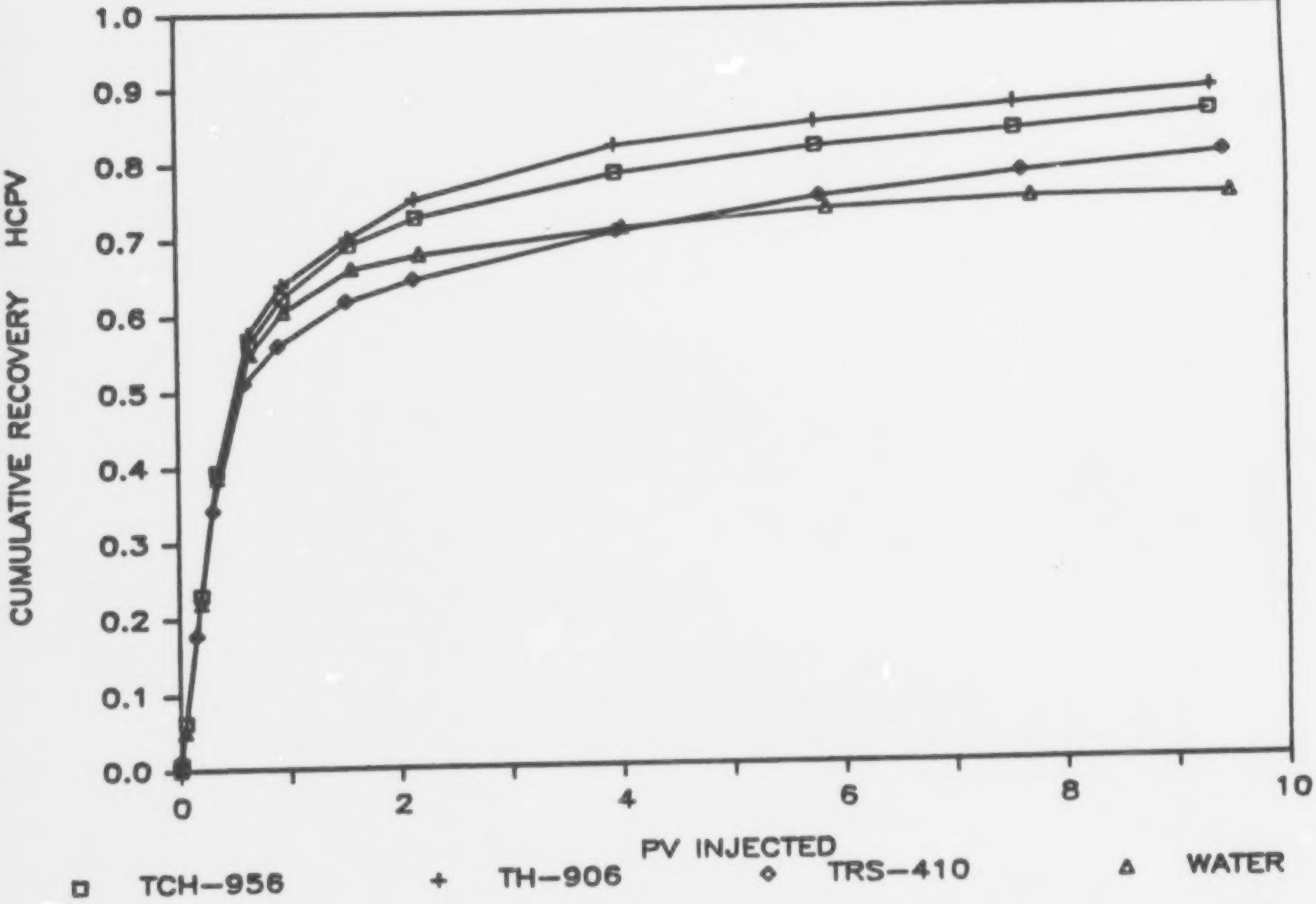


FIGURE 4-5

PELICAN WATER—OIL RATIO
AT 200C

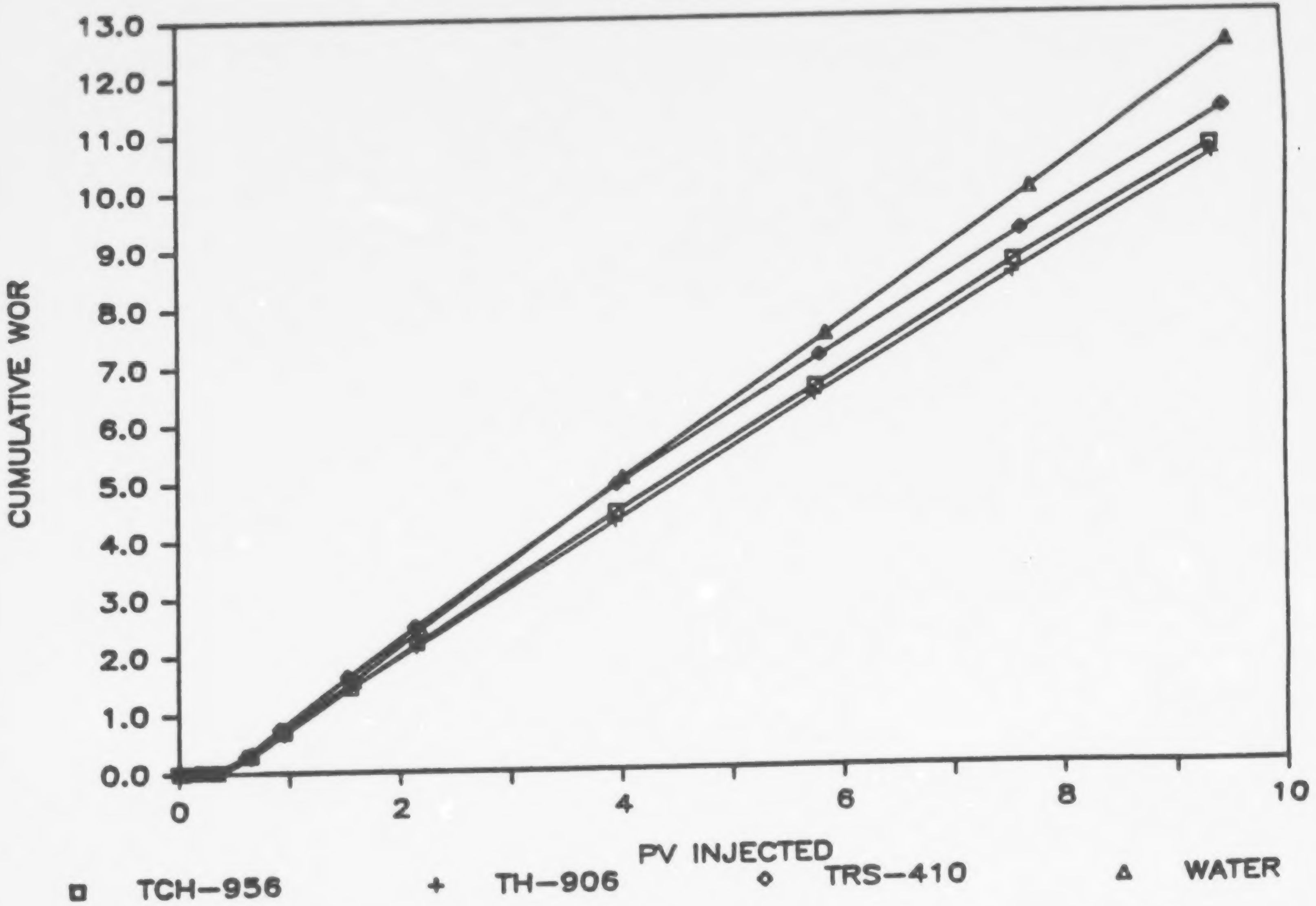


FIGURE 4-6

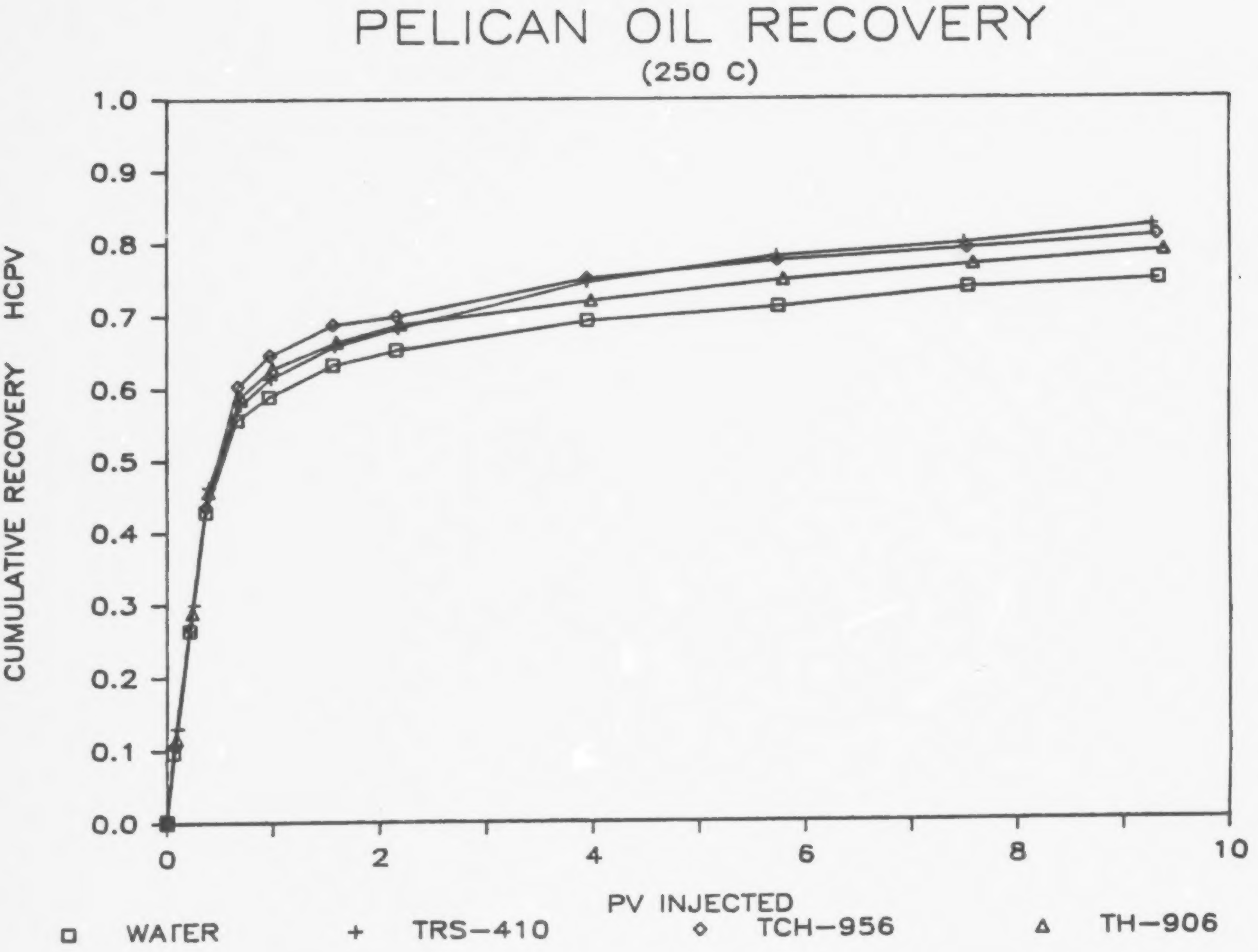

PELICAN OIL RECOVERY
(250 C)
CUMULATIVE RECOVERY HCPV
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
PV INJECTED
□ WATER
+ TRS-410
◇ TCH-956
△ TH-906

FIGURE 4-7

PELICAN WATER—OIL RATIO

(250 C)

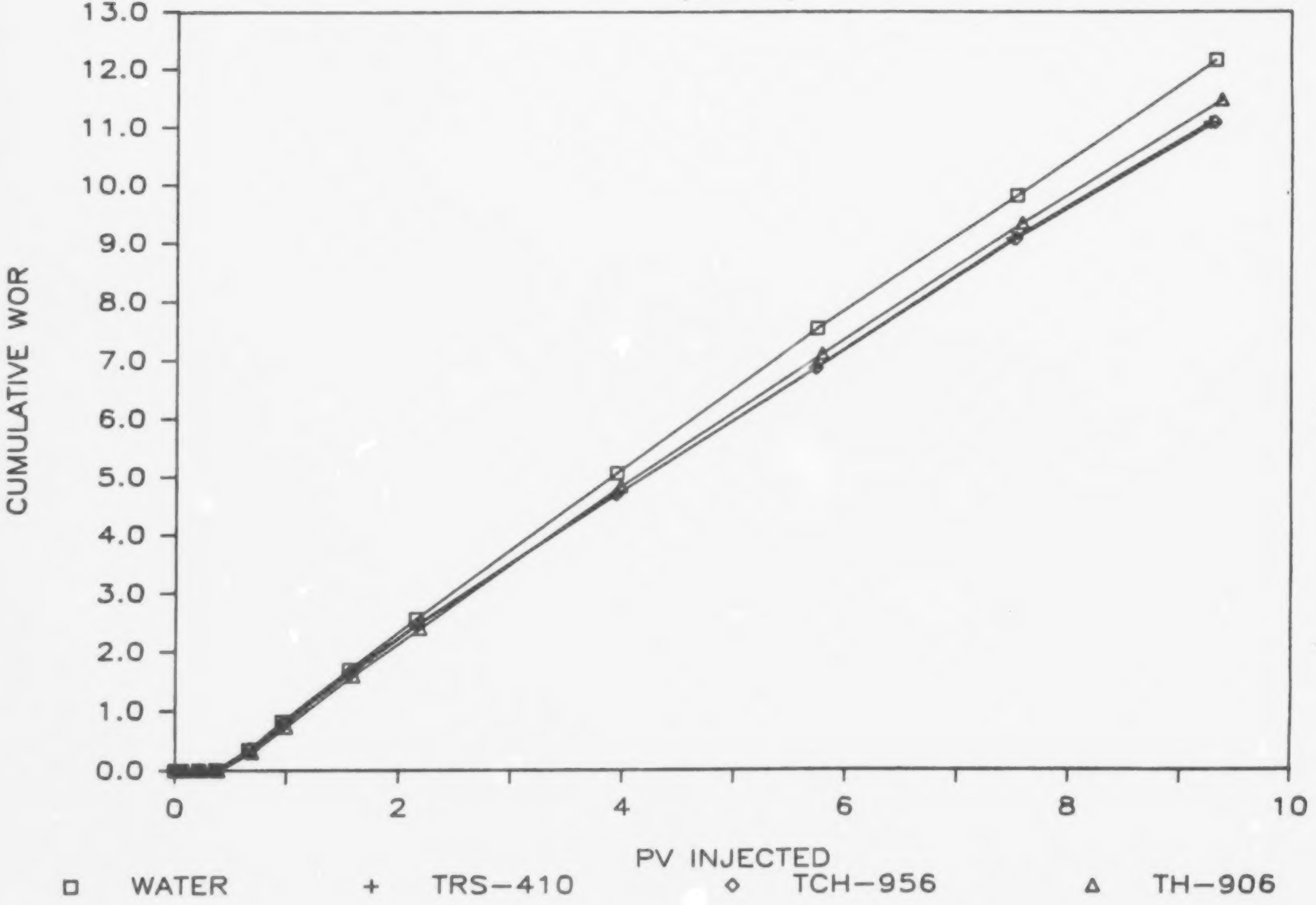


FIGURE 4-8

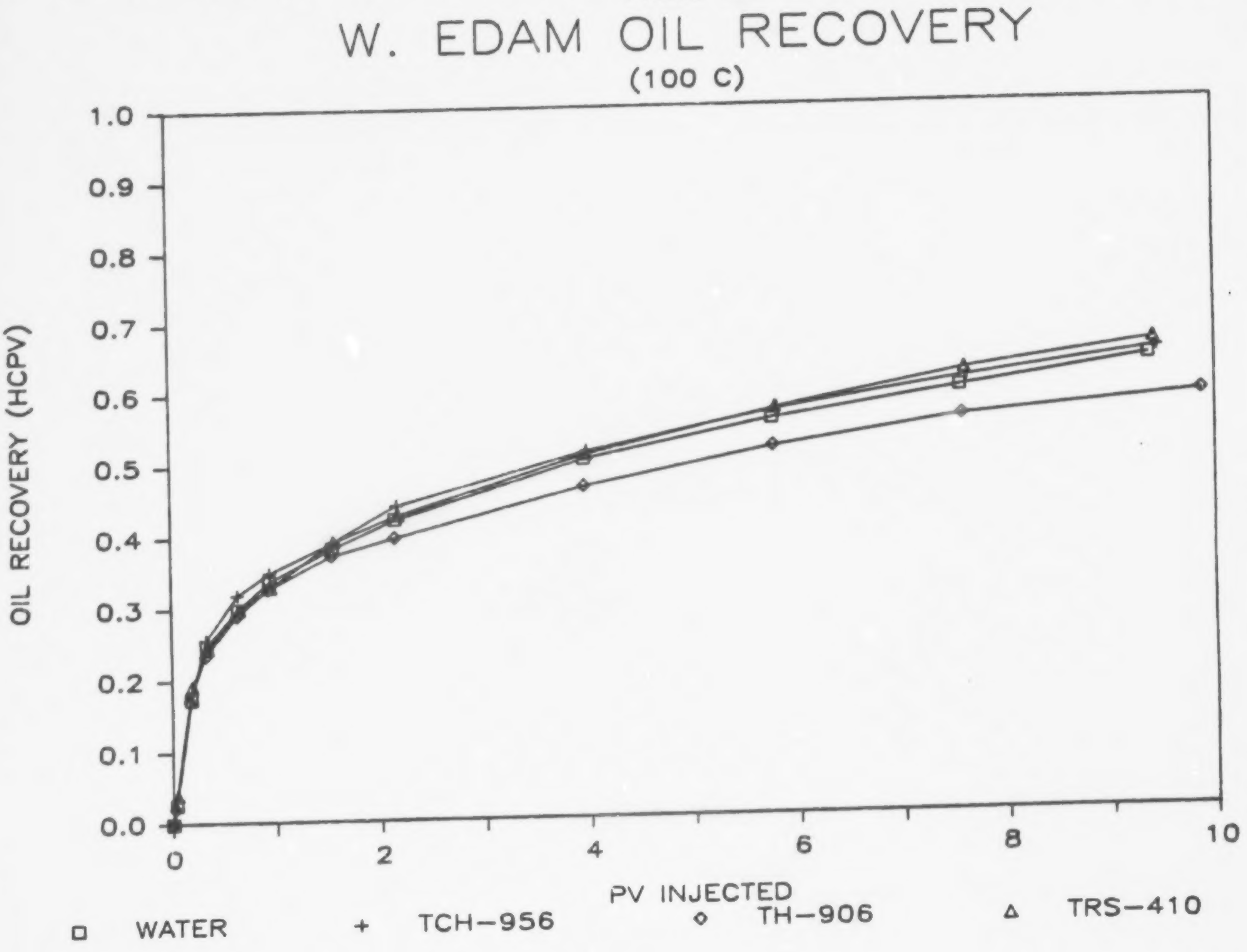

W. EDAM OIL RECOVERY
(100 C)
OIL RECOVERY (HCPV)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
2
4
6
8
10
PV INJECTED
□ WATER
+ TCH-956
◇ TH-906
△ TRS-410

FIG E 4

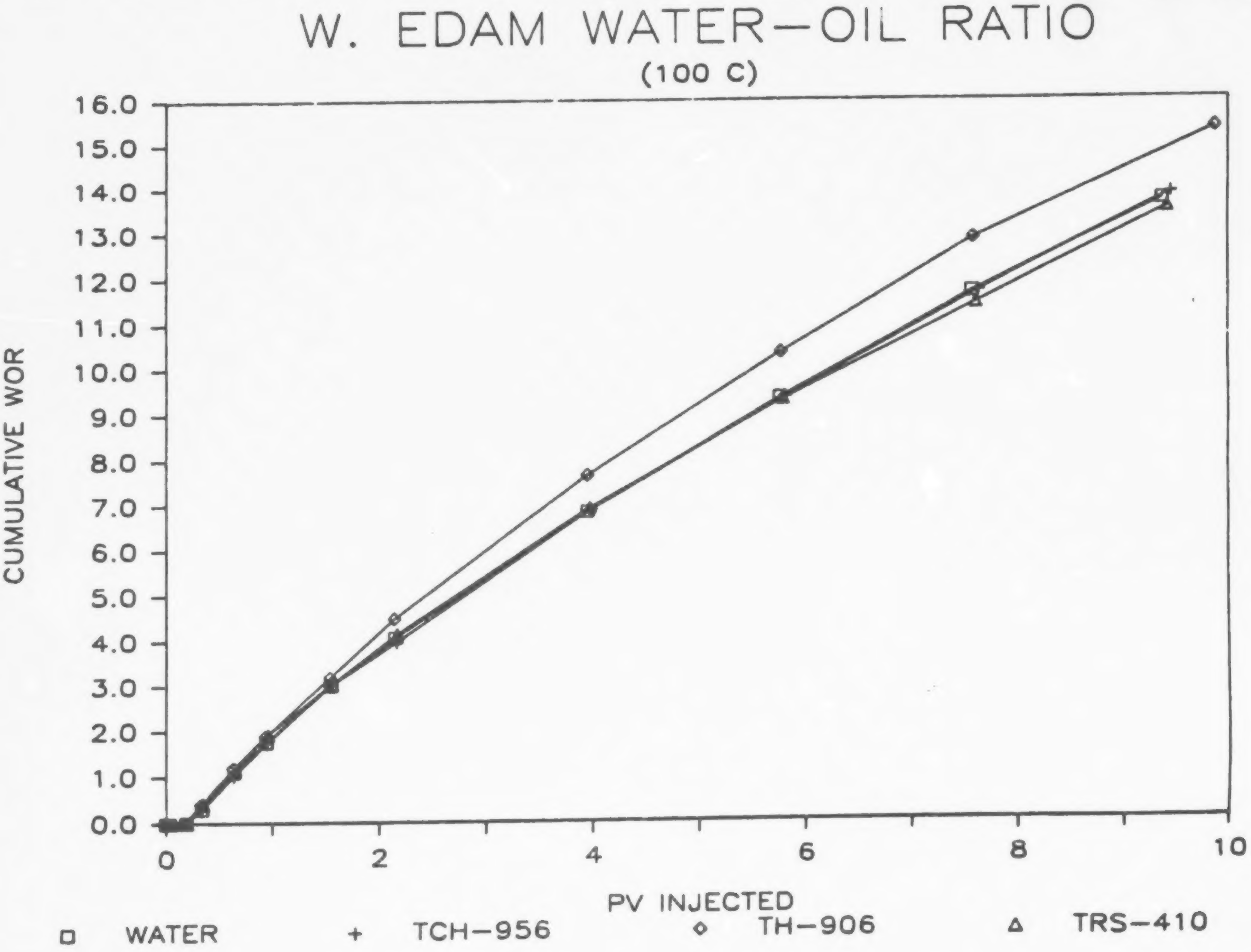

W. EDAM WATER—OIL RATIO
(100 C)
CUMULATIVE WOR
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
2
4
6
8
10
PV INJECTED
□ WATER
+ TCH—956
◇ TH—906
△ TRS—410

FIGURE 4-10

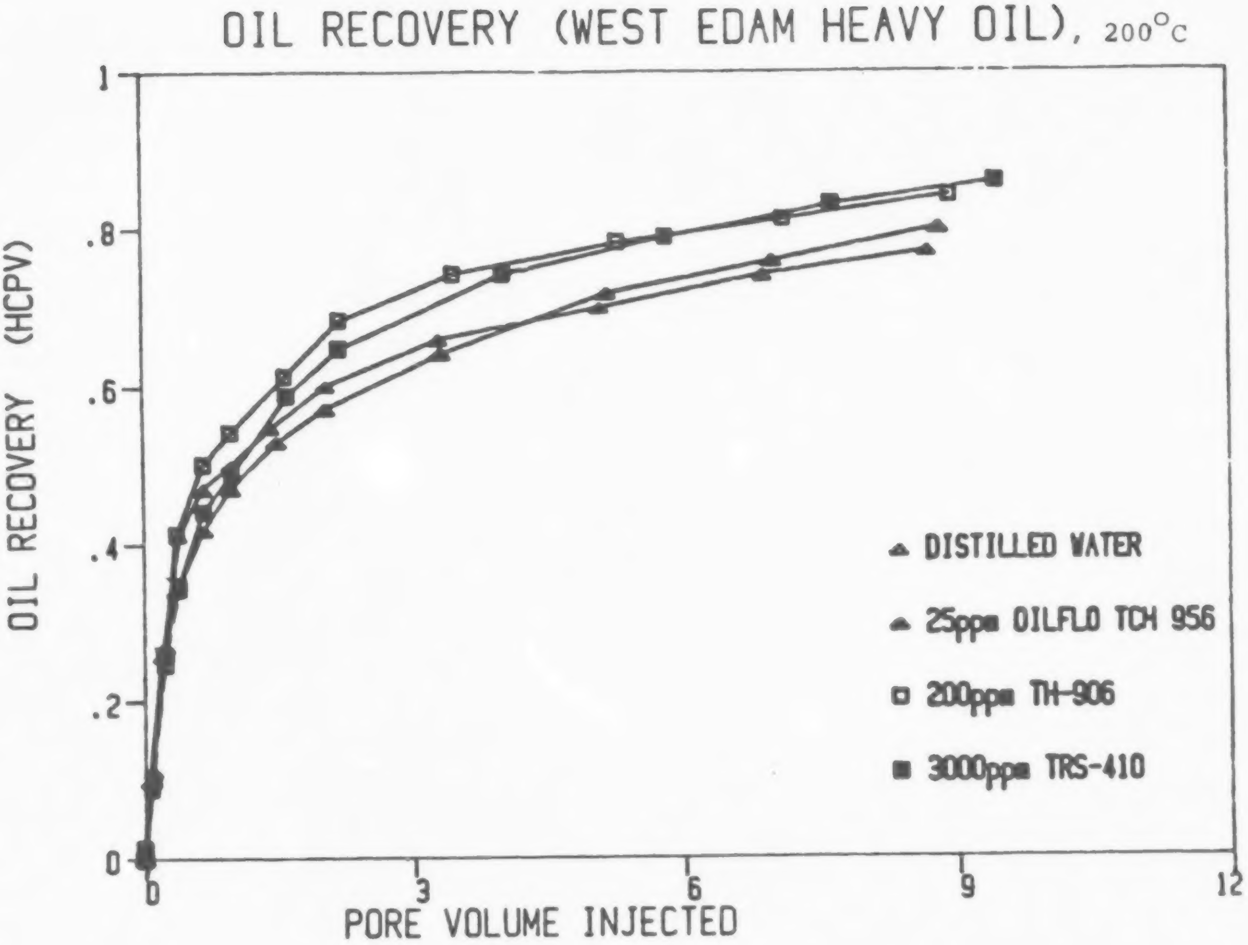

OIL RECOVERY (WEST EDAM HEAVY OIL), 200°C
OIL RECOVERY (HCPV)
1
.8
.6
.4
.2
0
0
3
6
9
12
PORE VOLUME INJECTED
▲ DISTILLED WATER
▲ 25ppm OILFLO TCH 956
□ 200ppm TH-906
■ 3000ppm TRS-410

FIGURE 4-11

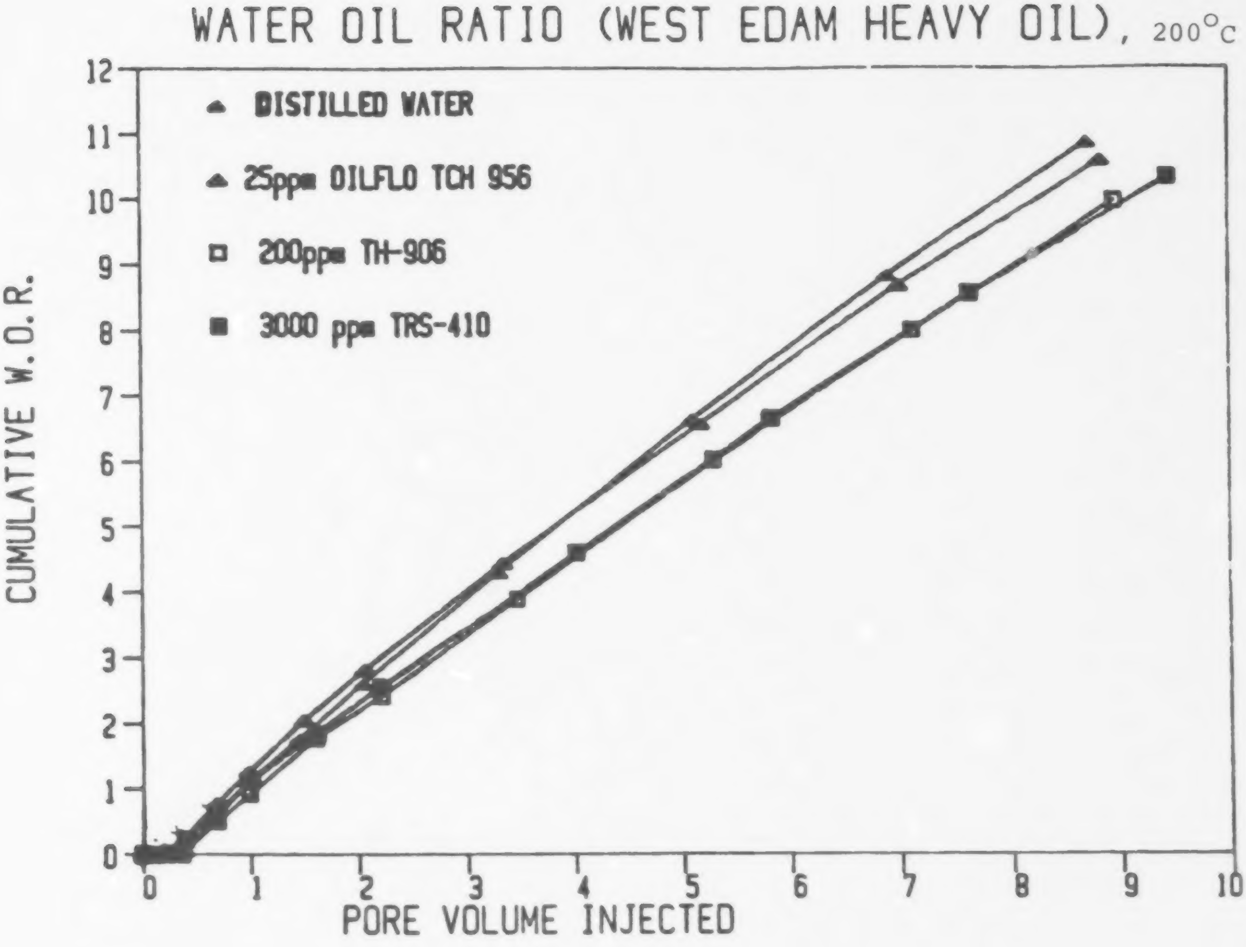

WATER OIL RATIO (WEST EDAM HEAVY OIL), 200°C
CUMULATIVE W.O.R.
PORE VOLUME INJECTED
DISTILLED WATER
25ppm OILFLO TCH 956
200ppm TH-906
3000 ppm TRS-410
0
1
2
3
4
5
6
7
8
9
10
11
12

FIGURE 4-12

W. EDAM OIL RECOVERY

(250 C)

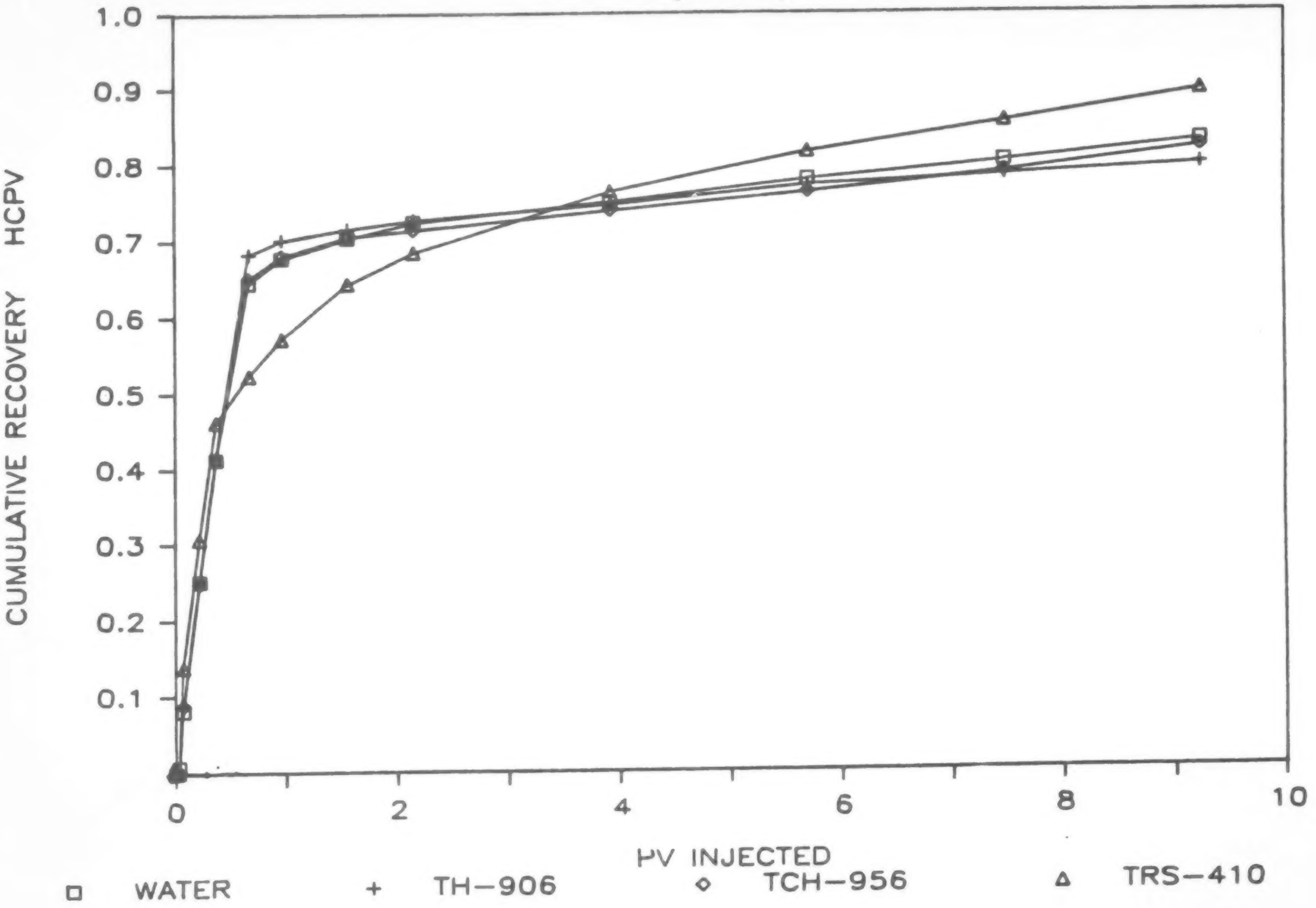
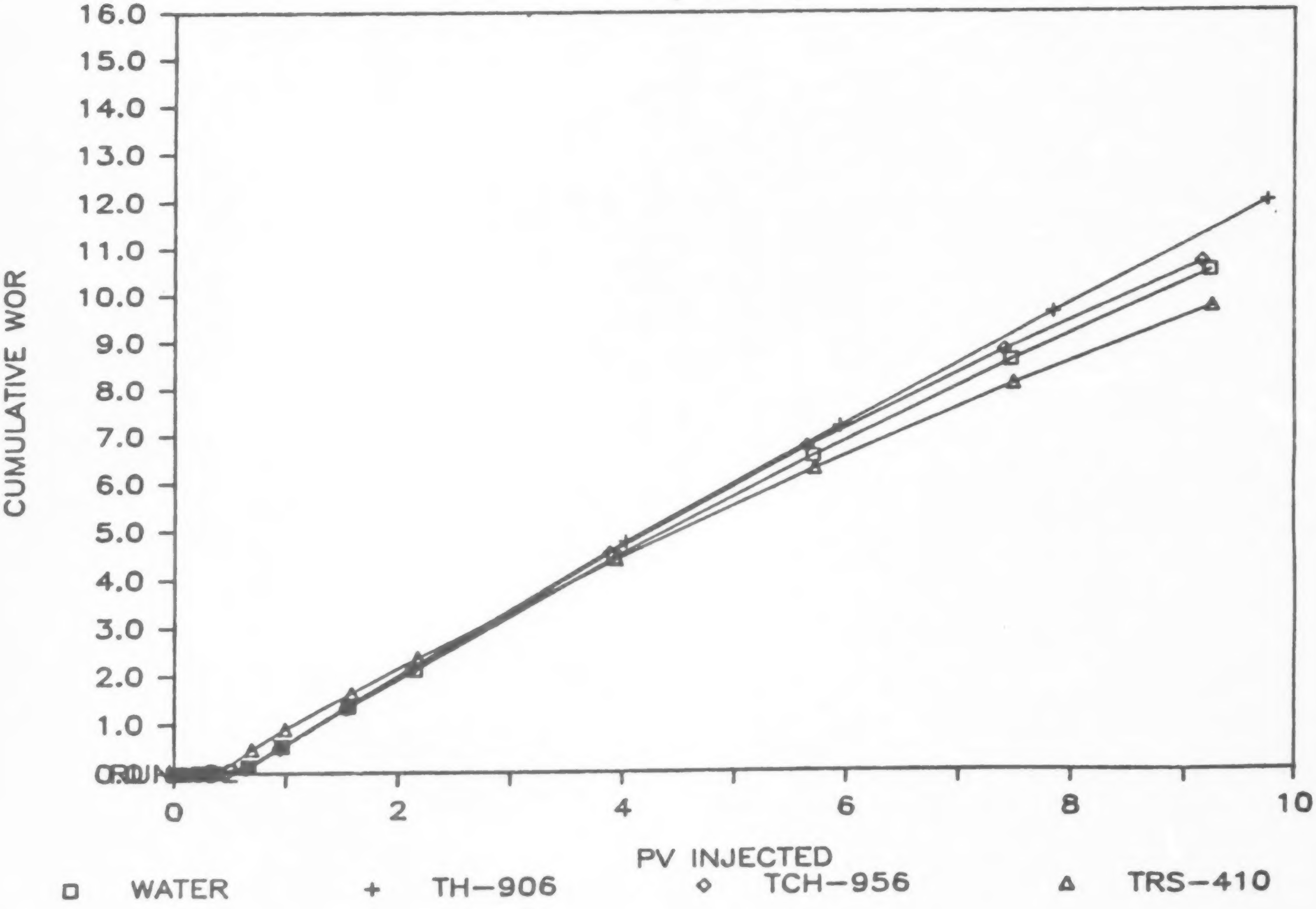


FIGURE 4-13

W.EDAM WATER—OIL RATIO
(250 C)



For the Pelican Lake oil, the data suggests a slight improvement in the displacement due to the presence of the additives in the injection fluid. Thus, few percent increase in oil recovery, and a corresponding decrease in water-oil ratios was observable at each of the three operating temperatures.

The Thermoflood 906 solution resulted in the highest recoveries at 100 and 200°C. But there was generally no overwhelming advantage of any of the additives over the other two.

Due to the lack of a strong performance of any of the additives, in comparison with plain water injection, dissolving the additives in the connate water was also tested in a set of experiments at 200°C, using Pelican Lake oil. In this set of runs, the freshly packed sand cores were first saturated with the additive solution, instead of brine. The additive solution was then displaced, with Pelican Lake oil, down to its irreducible level. The experiments were then continued following the normal procedure. The results of this set of experiments are displayed in Figures 4-14 and 4-15. Some improvement, over the normal mode of additive application, may be observed. The improvement, however, is not so significant as to suggest that additive adsorption in this relatively unrealistic mode of application is a dominant factor in the displacement mechanism.

In summary, examining all the displacement experiments results, it is clear that the effect of any of the three additives, in improving oil recovery, is marginal. The petroleum sulfonate additive TRS-410 shows relatively better interaction, than the other two agents, with the W. Edam oil at the three different operating temperatures. The thin film spreading agent Thermoflood-906 appears to be more suited for the Pelican Lake oil.

FIGURE 4-14

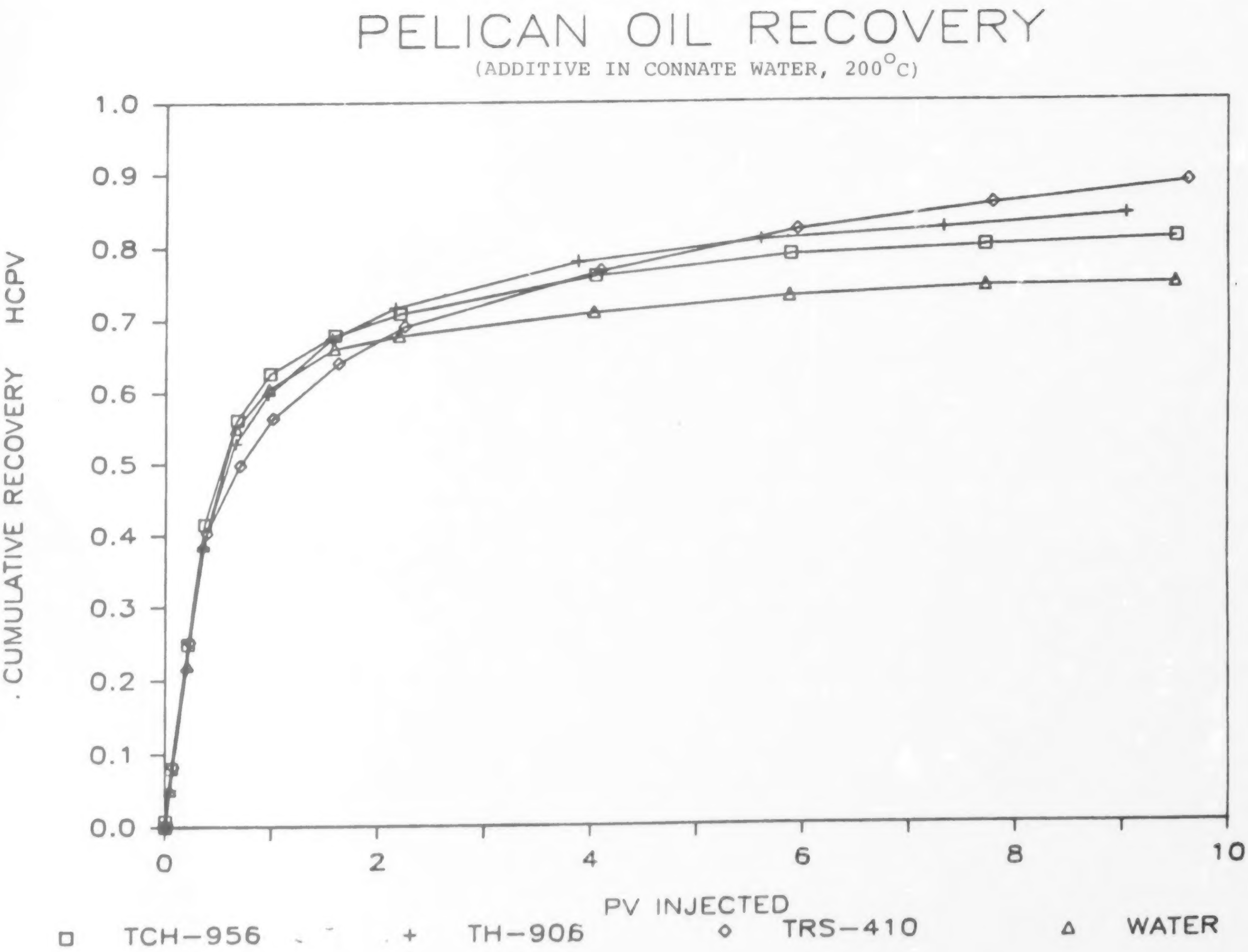
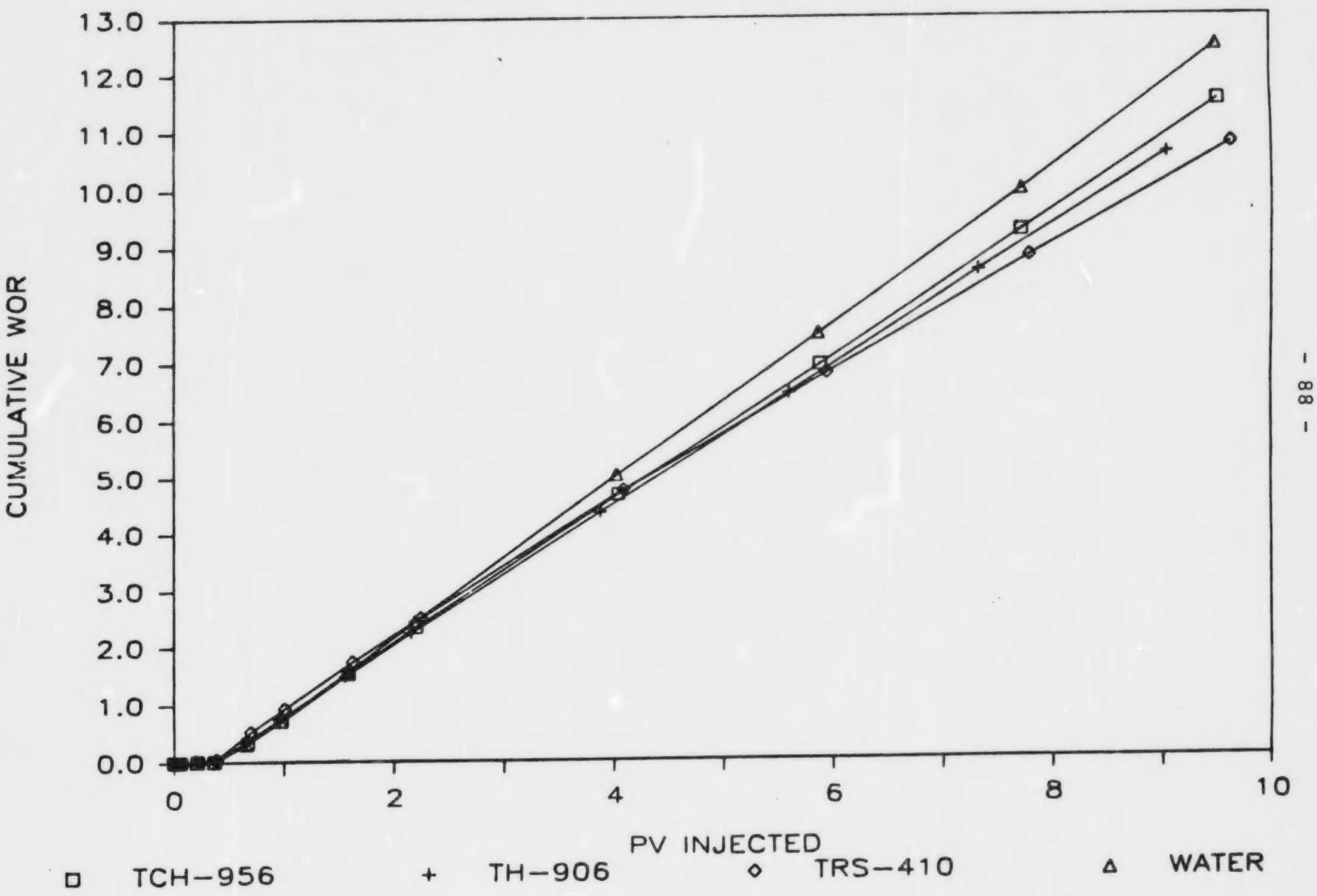

PELICAN OIL RECOVERY
(ADDITIVE IN CONNATE WATER, 200°C)
CUMULATIVE RECOVERY HCPV
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
PV INJECTED
□ TCH-956
+ TH-906
◇ TRS-410
△ WATER

FIGURE 4-15

PELICAN WATER—OIL RATIO

(ADDITIVE IN CONNATE WATER, 200°C)



4.3 Effect of Temperature

It was interesting to assess the effect of temperature based on the displacement results. Figures 4-16 to 4-23 highlight this effect, as reflected on oil recovery and water-oil ratios, for the Pelican Lake oil. The corresponding data for the W. Edam oil displayed in Figures 4-24 to 4-31.

In the case of Pelican Lake oil, the temperature has a very small effect on the recovery characteristics, as can be observed with each of the four injection fluids (water and the three additive solutions). For the West Edam oil, on the other hand, a large increase in oil recovery and decrease of oil-water ratios is noticeable with an increase in the operating temperature, particularly from 100°C to 200°C. An increase in the operating temperature from 200°C to 250°C shows a less pronounced effect, on the W. Edam oil displacement, in most of the cases. These interesting trends are readily explained by the effect of temperature on the viscosity of the two different oils.

The temperature increase, from 100°C to 250°C, has little effect on the Pelican Lake oil because of its relatively low viscosity at 100°C and lower rate of viscosity decreased with increased temperature to 250°C. Thus the recovery of this oil is high at 100°C, with little further benefits derived from a temperature increase. Conversely, the W. Edam oil is characterized by much higher viscosity at 100°C, which results in relatively lower oil recovery. An increase in temperature to 200°C, however, results in a pronounced decrease in viscosity and a corresponding increase in oil recovery.

FIGURE 4-16

PELICAN OIL RECOVERY

WATER

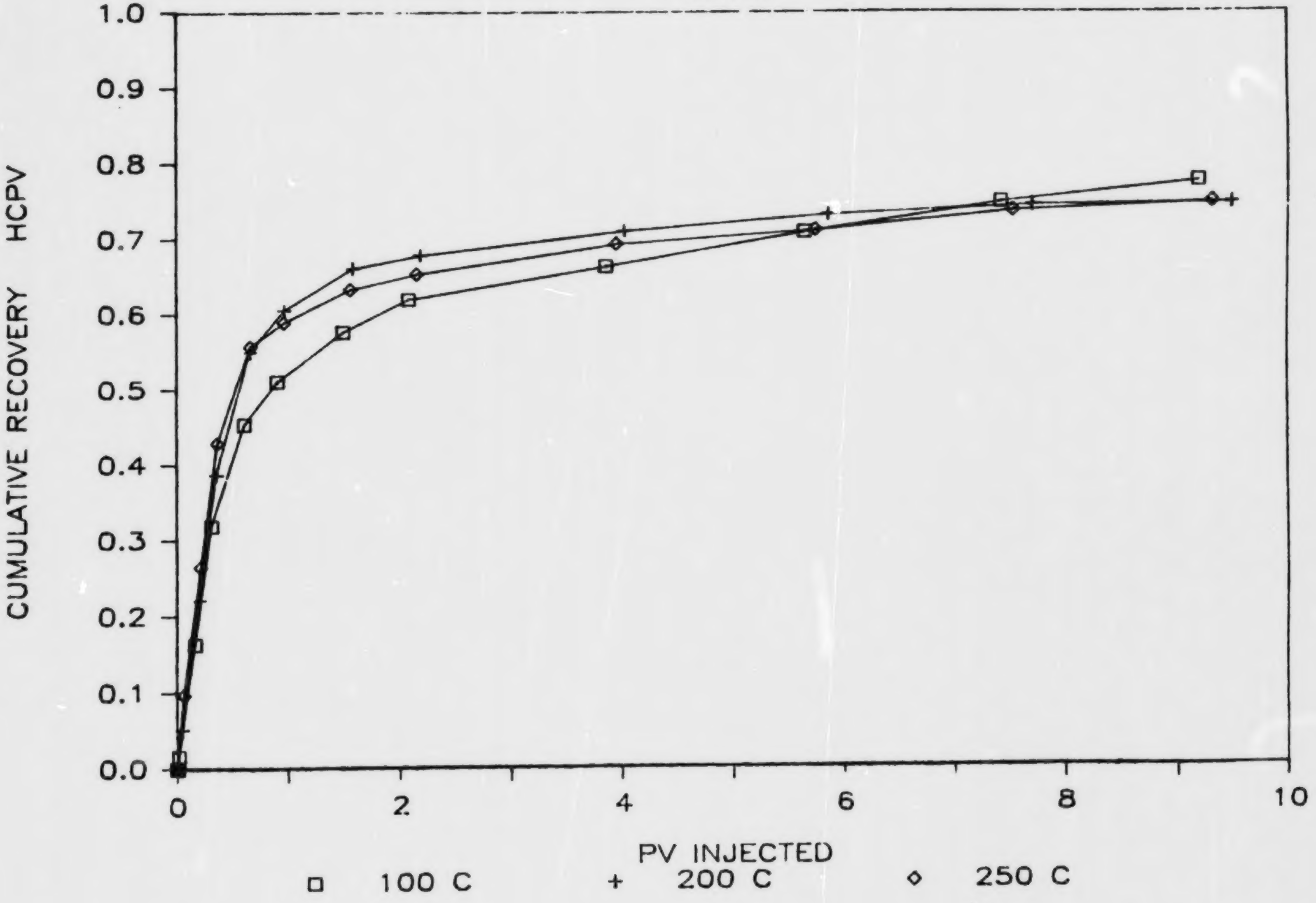


FIGURE 4-17

PELICAN WATER—OIL RATIO

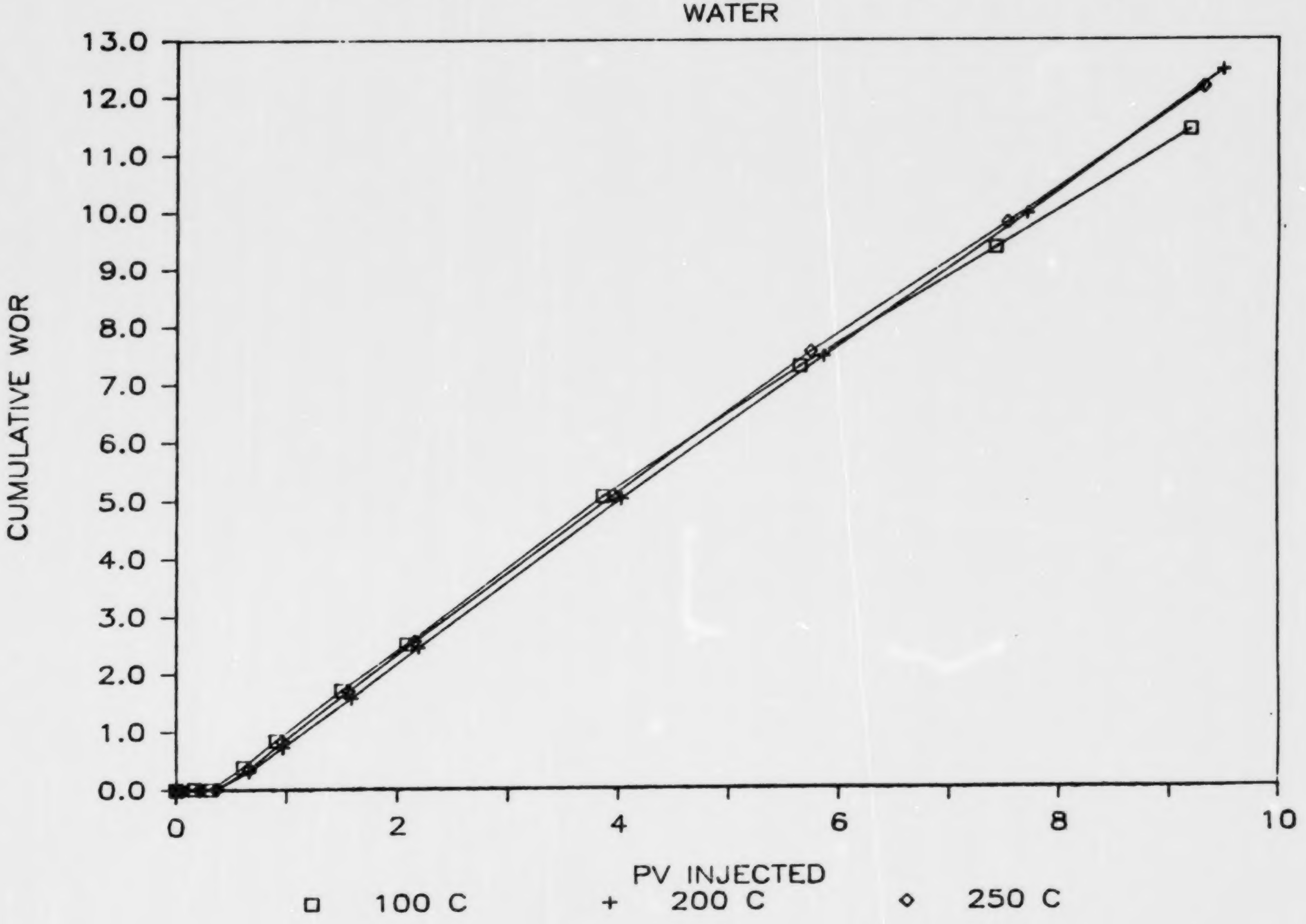
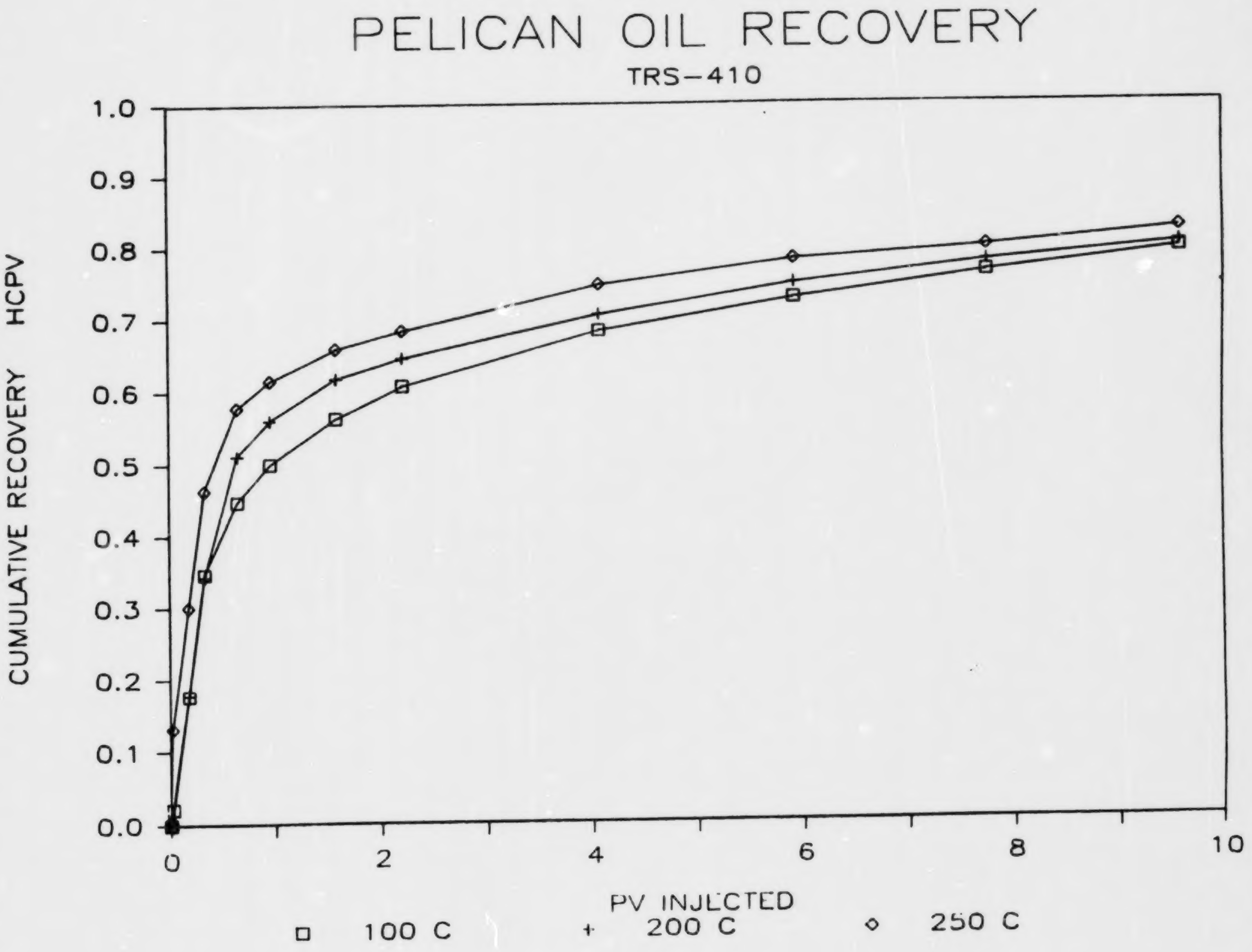


FIGURE 4-18



PELICAN OIL RECOVERY

TRS-410

FIGURE 4-19

PELICAN WATER—OIL RATIO

TRS—410

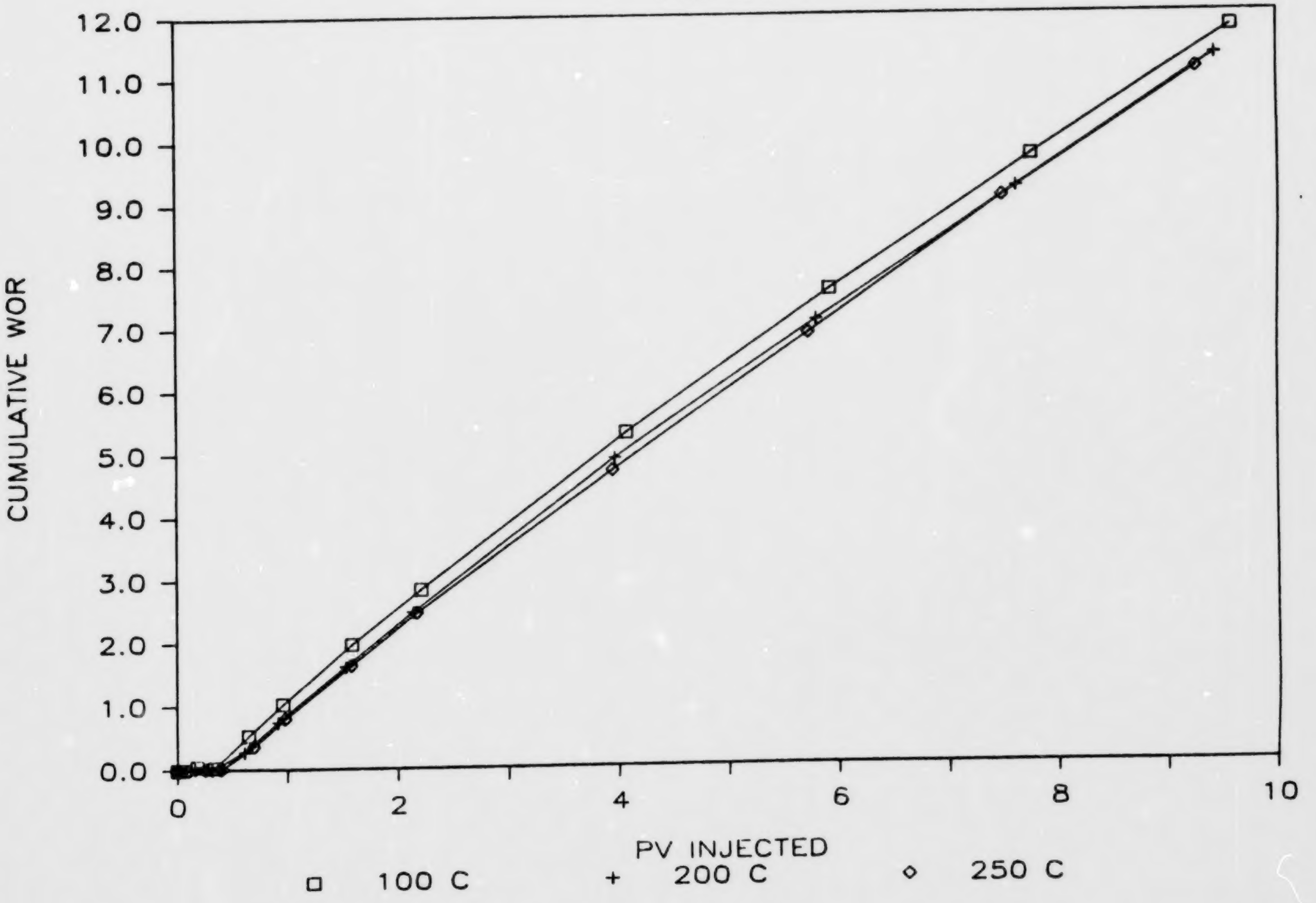


FIGURE 4-20

PELICAN OIL RECOVERY

TCH-956

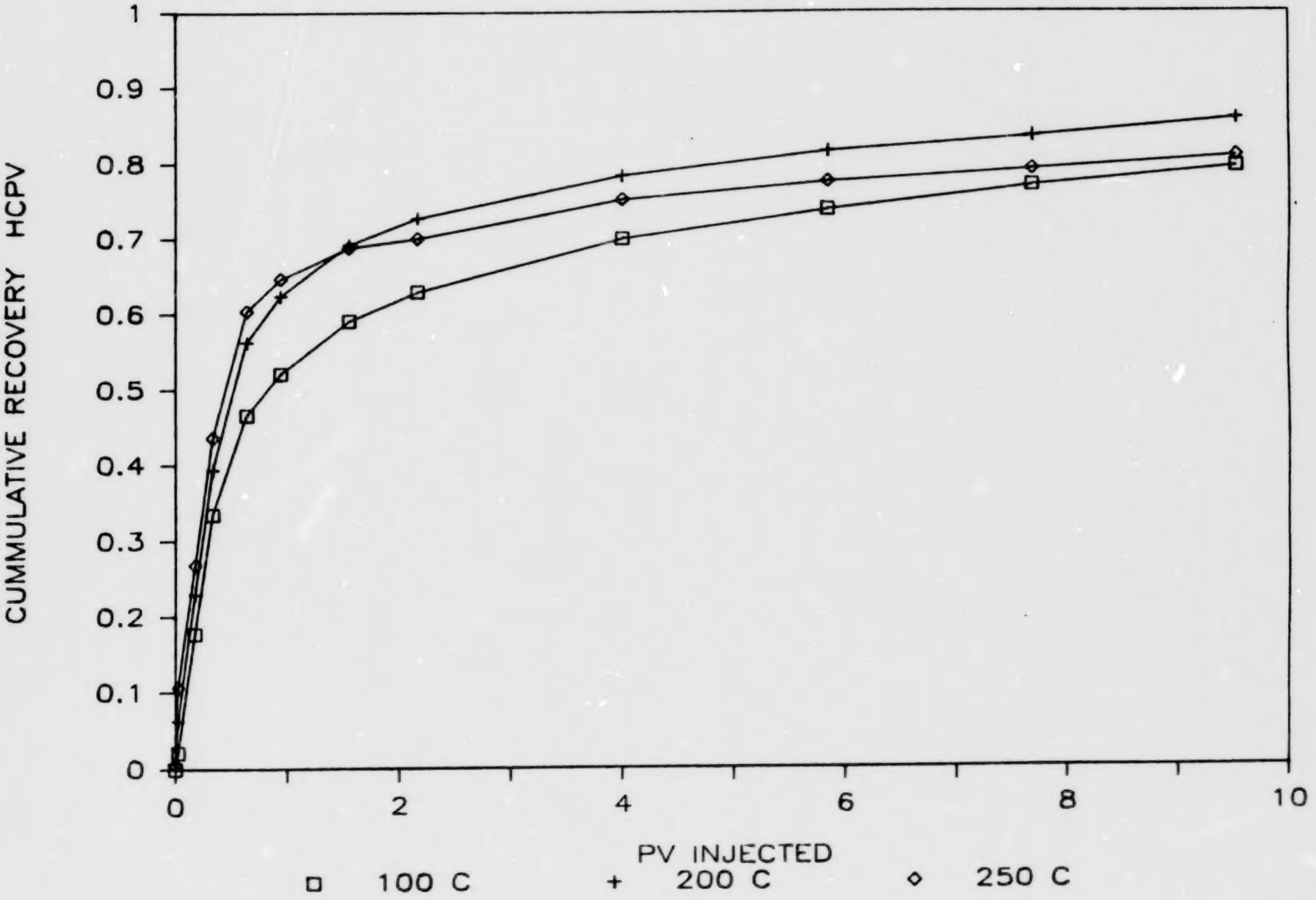


FIGURE 4-21

PELICAN WATER—OIL RATIO

TCH—956

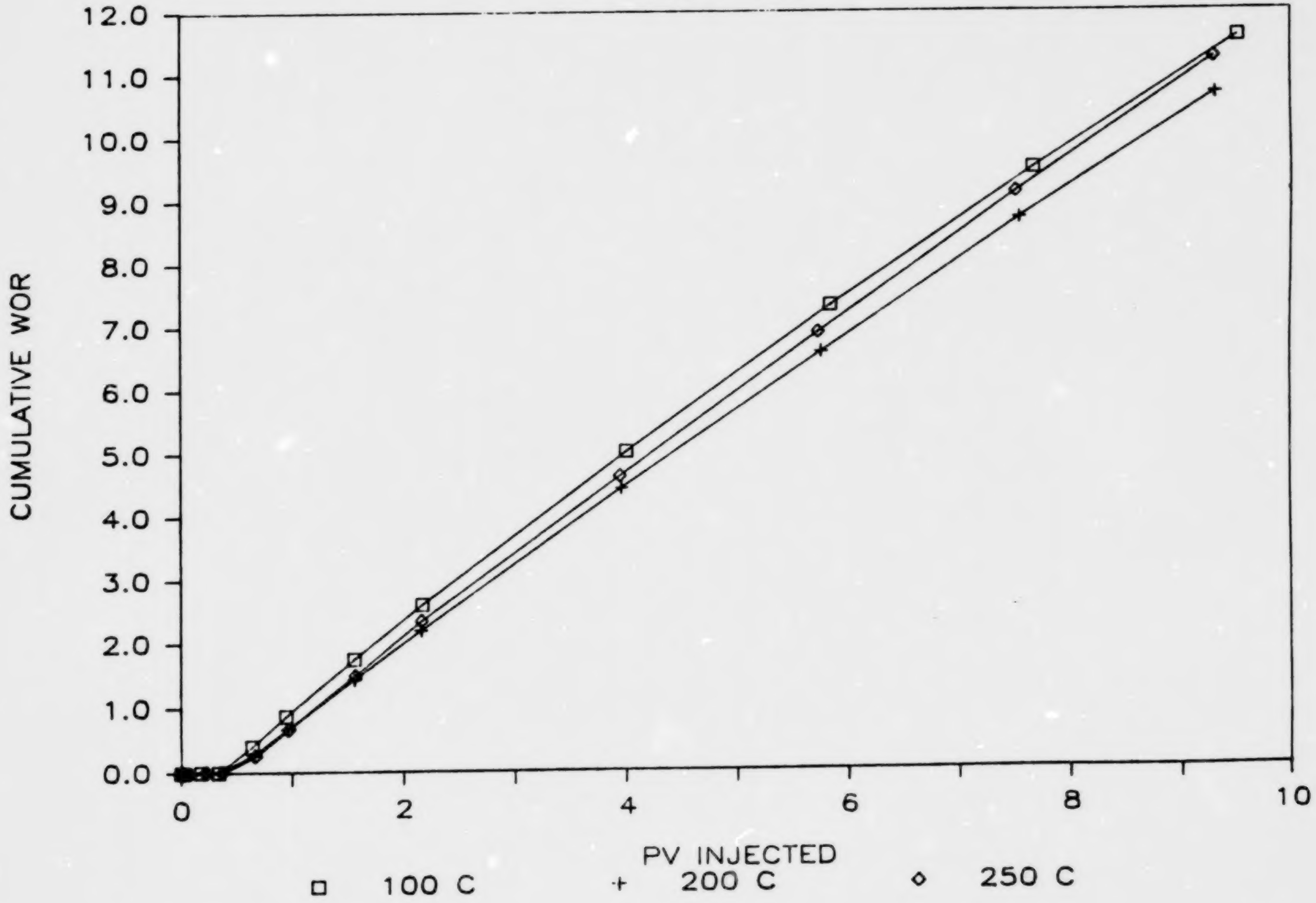


FIGURE 4-22

PELICAN OIL RECOVERY

TH-906

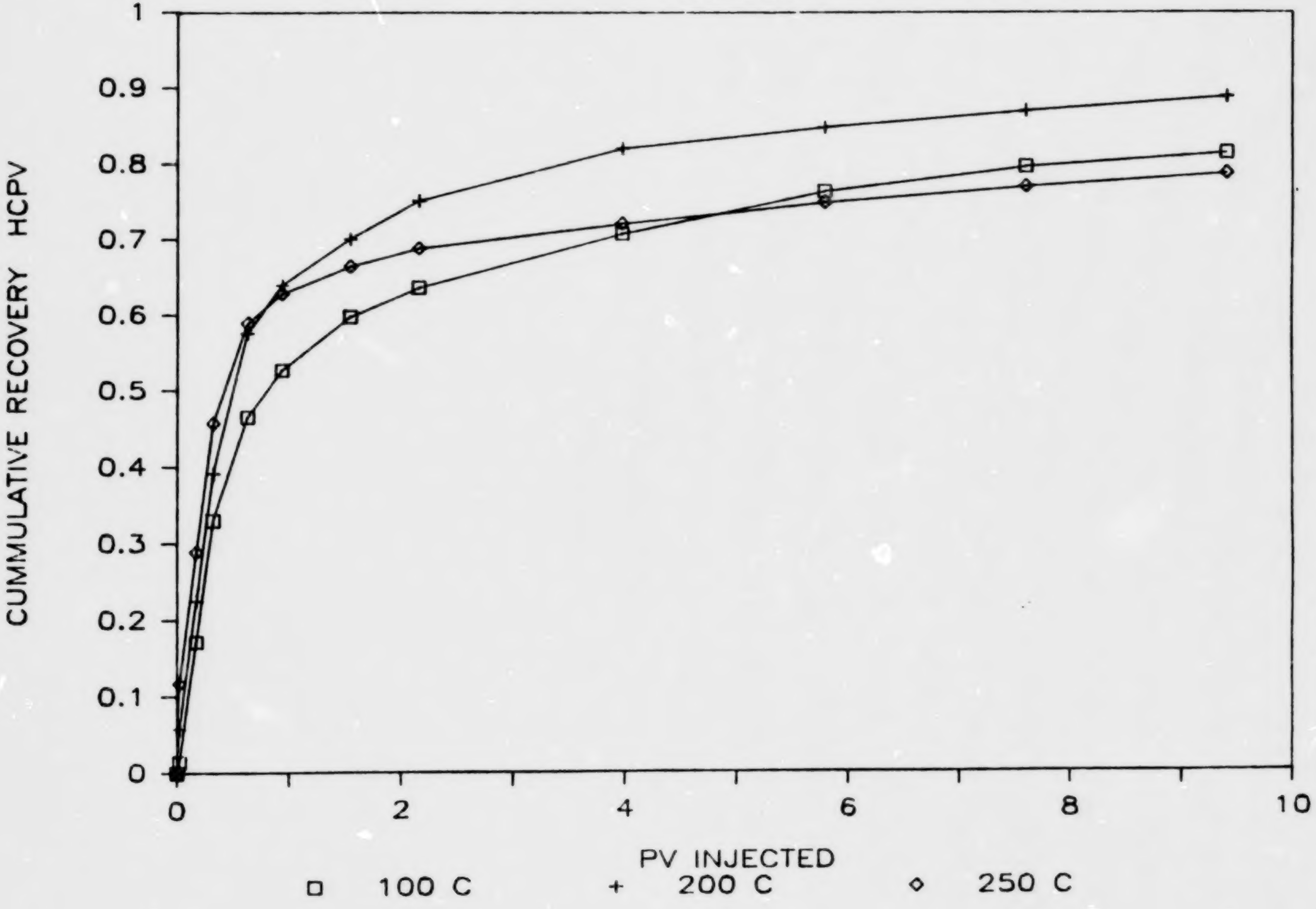


FIGURE 4-23

PELICAN WATER—OIL RATIO

TH—906

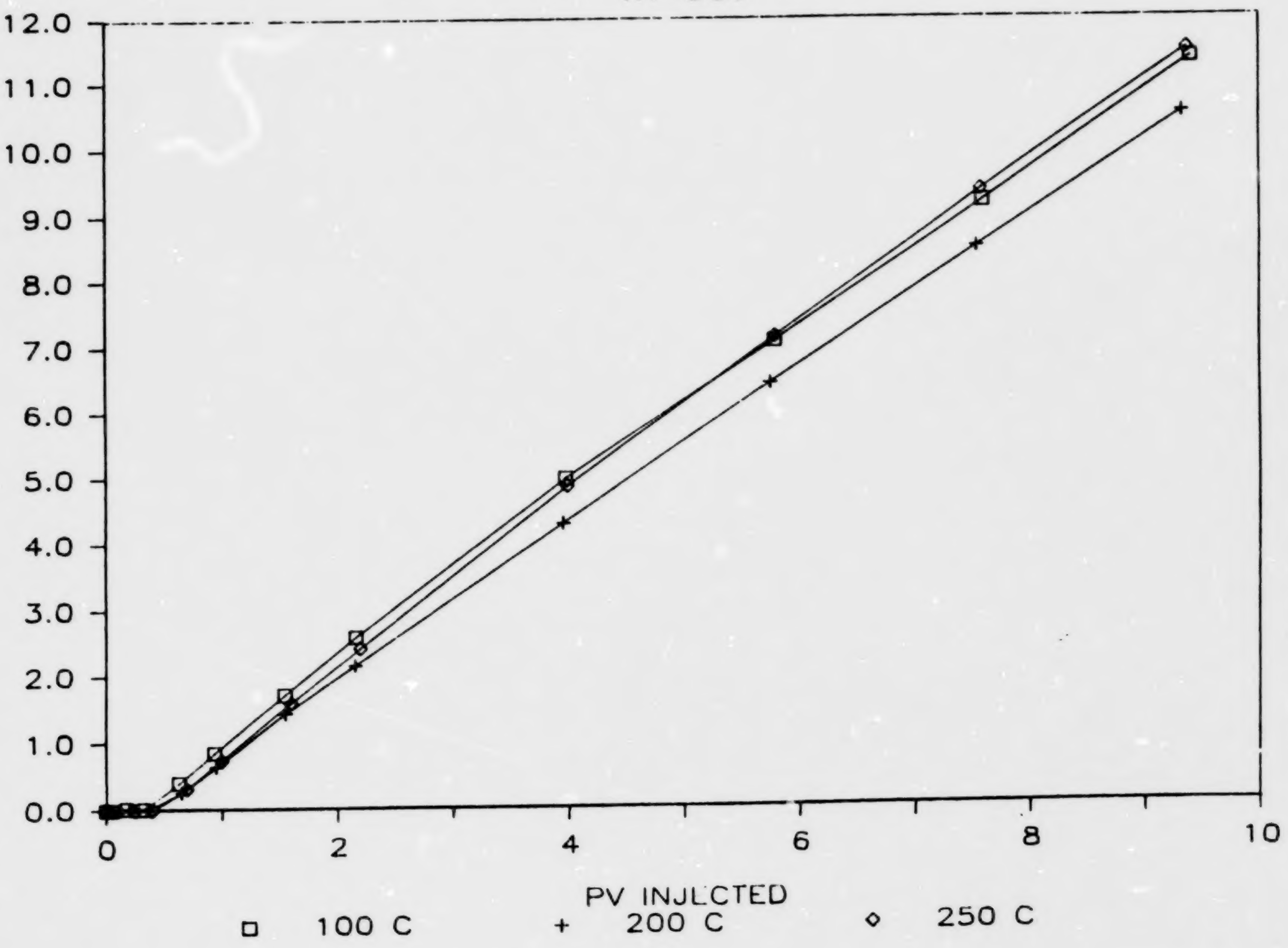


FIGURE 4-24

W. EDAM OIL RECOVERY

WATER

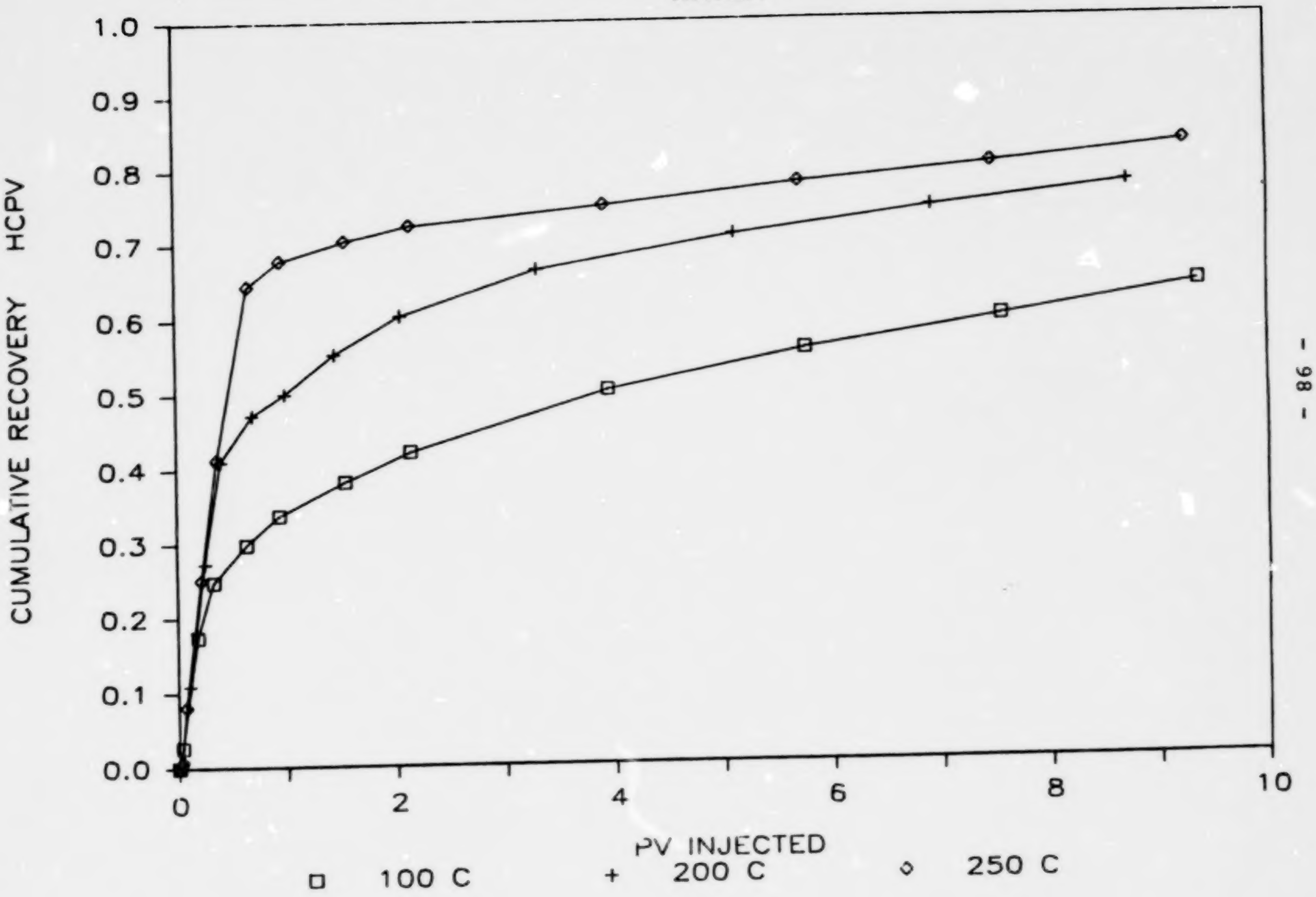


FIGURE 4-25

W.EDAM WATER—OIL RATIO

WATER

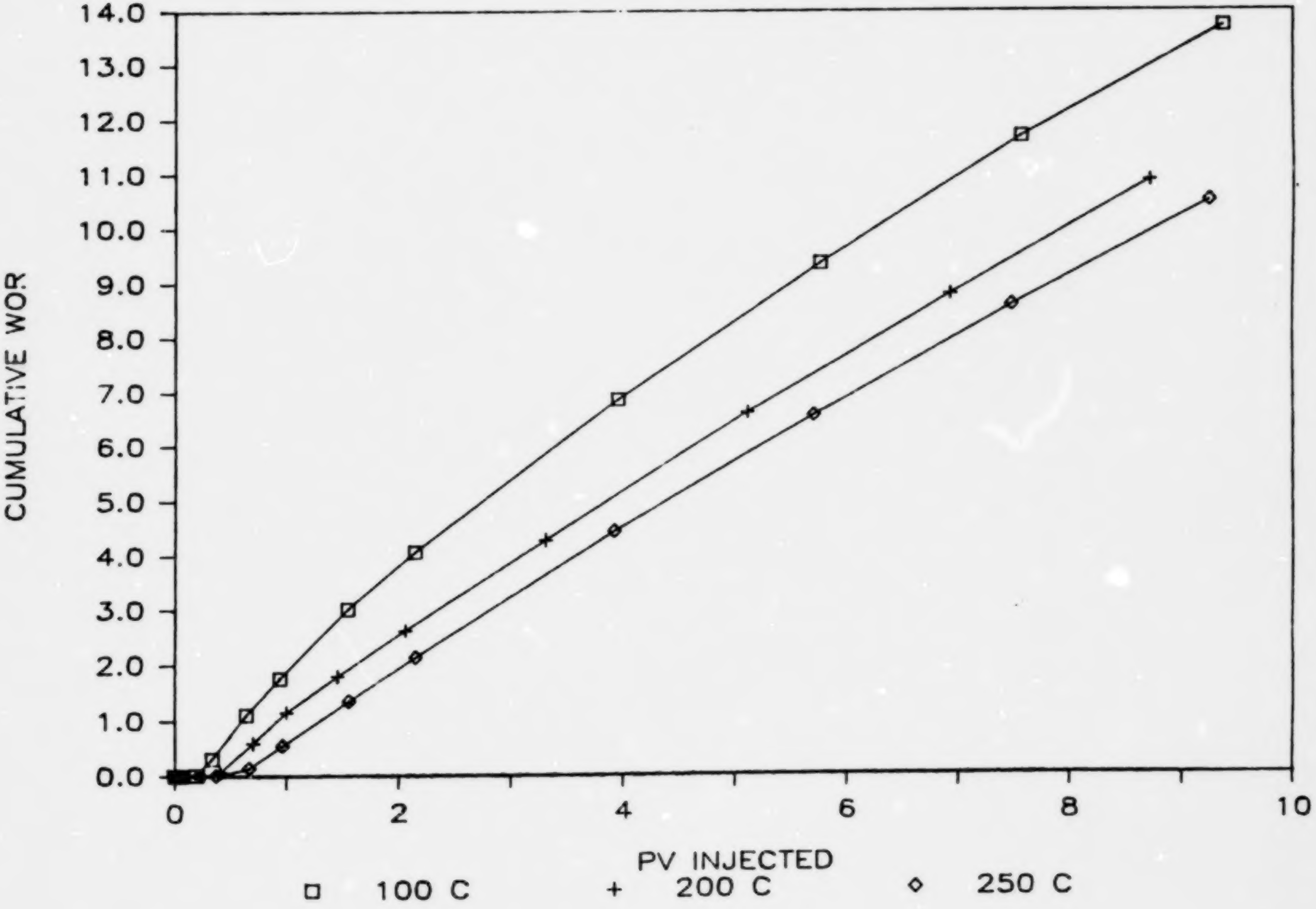


FIGURE 4-26

W.EDAM OIL RECOVERY

TRS–410

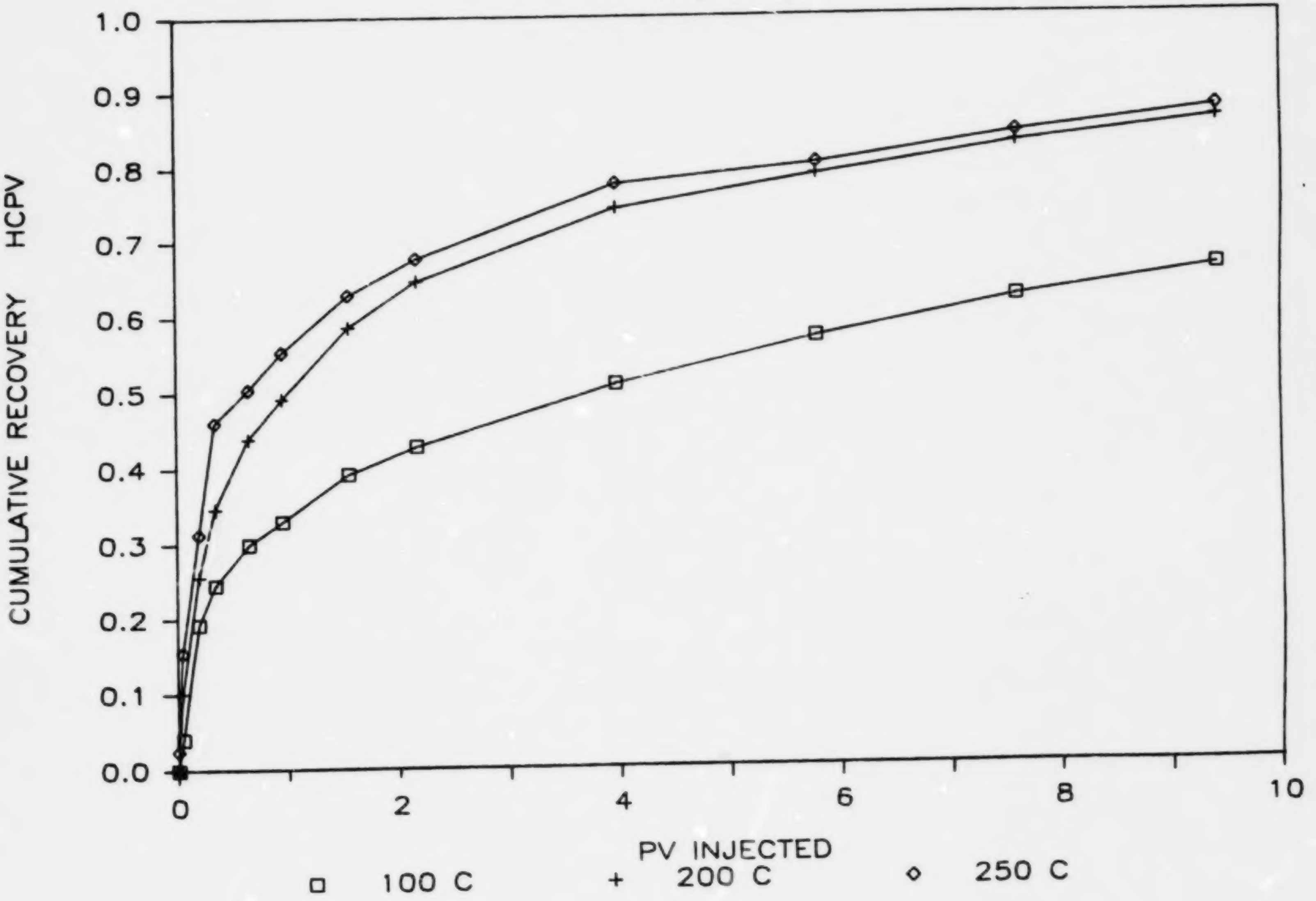


FIGURE 4-27

W.EDAM WATER—OIL RATIO

TRS—410

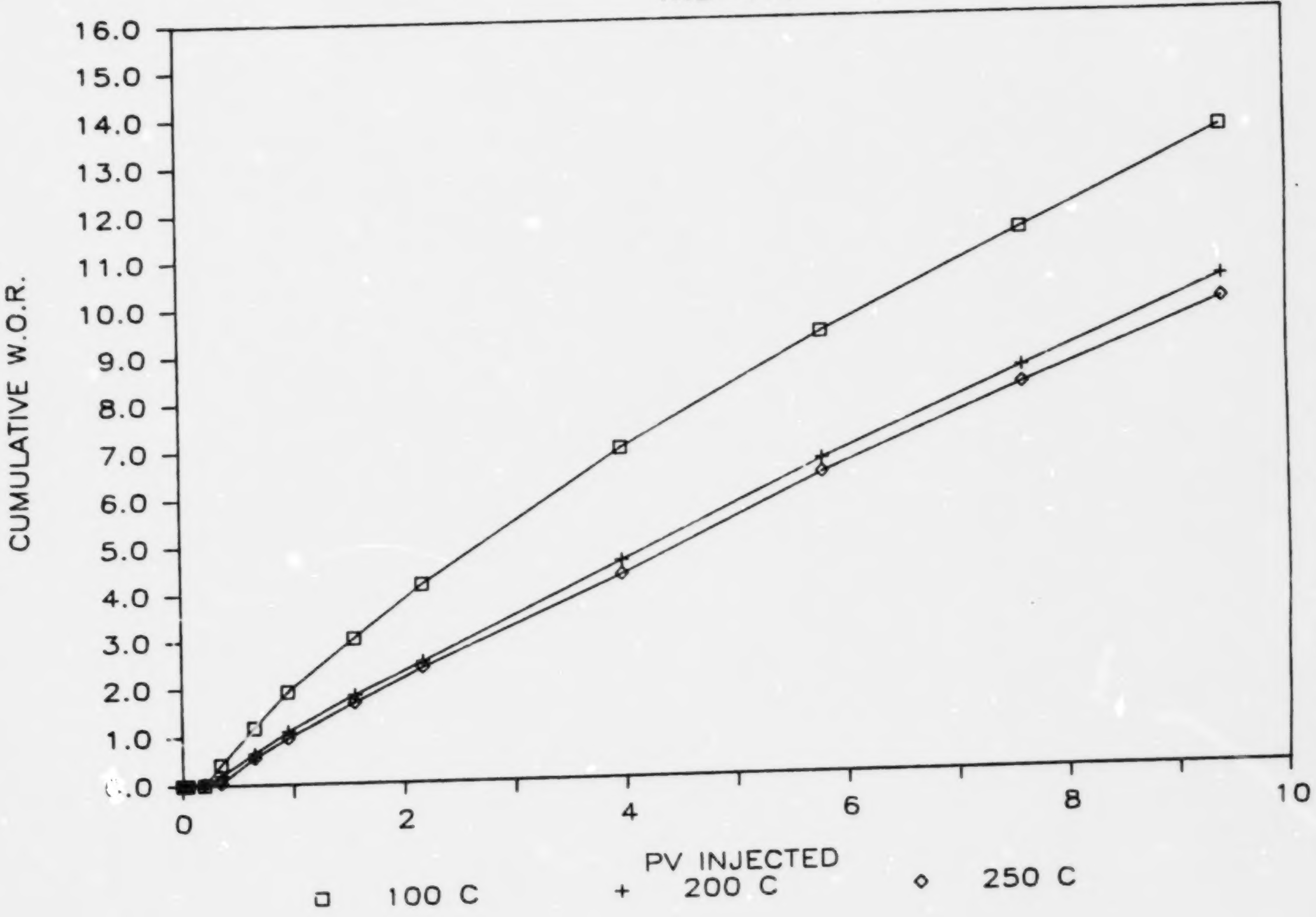


FIGURE 4-28

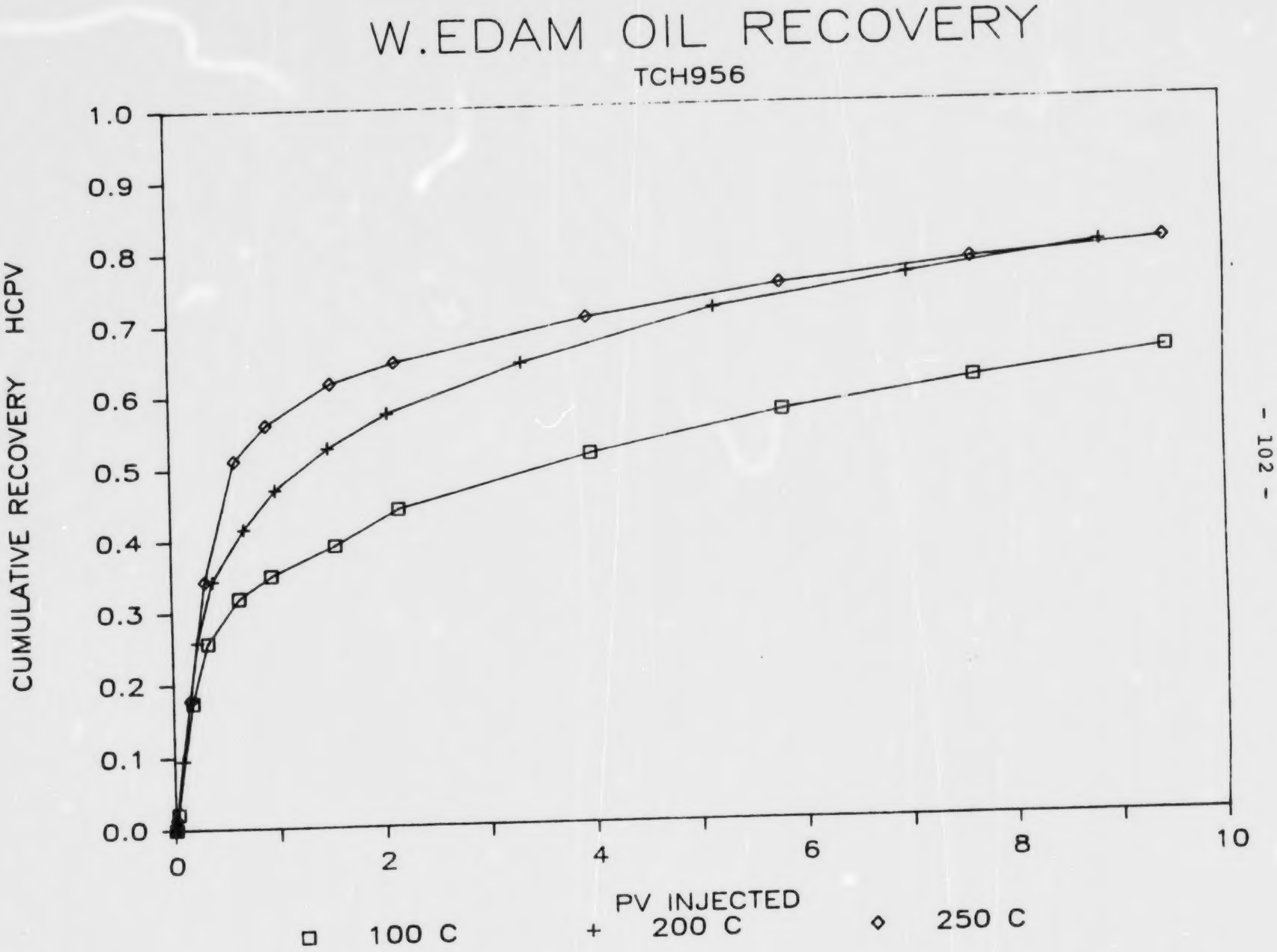

W.EDAM OIL RECOVERY
TCH956
CUMULATIVE RECOVERY HCPV
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
PV INJECTED
□ 100 C
+ 200 C
◇ 250 C

FIGURE 4-29

W.EDAM WATER—OIL RATIO

TCH—956

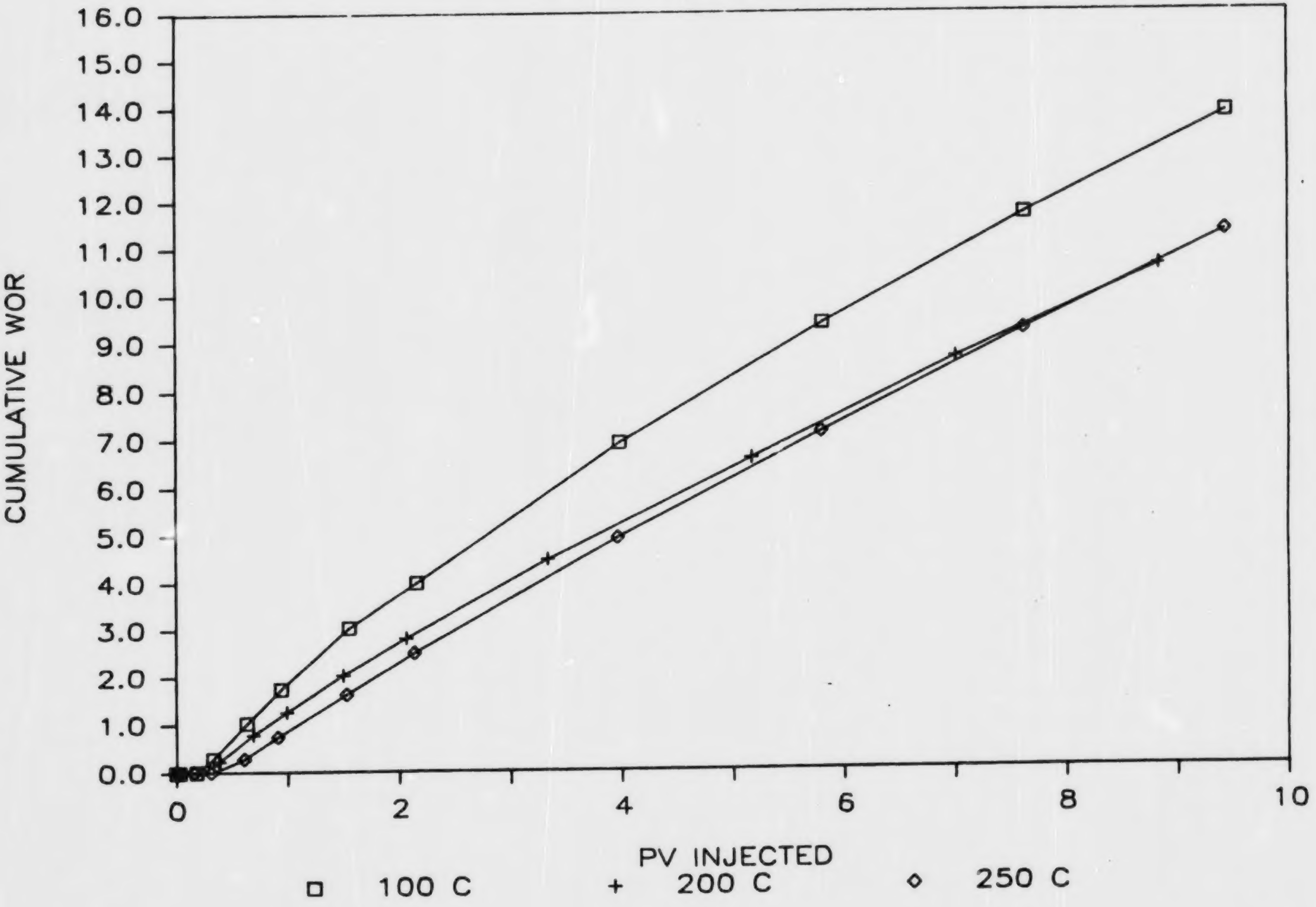


FIGURE 4-30

W.EDAM OIL RECOVERY

TH-906

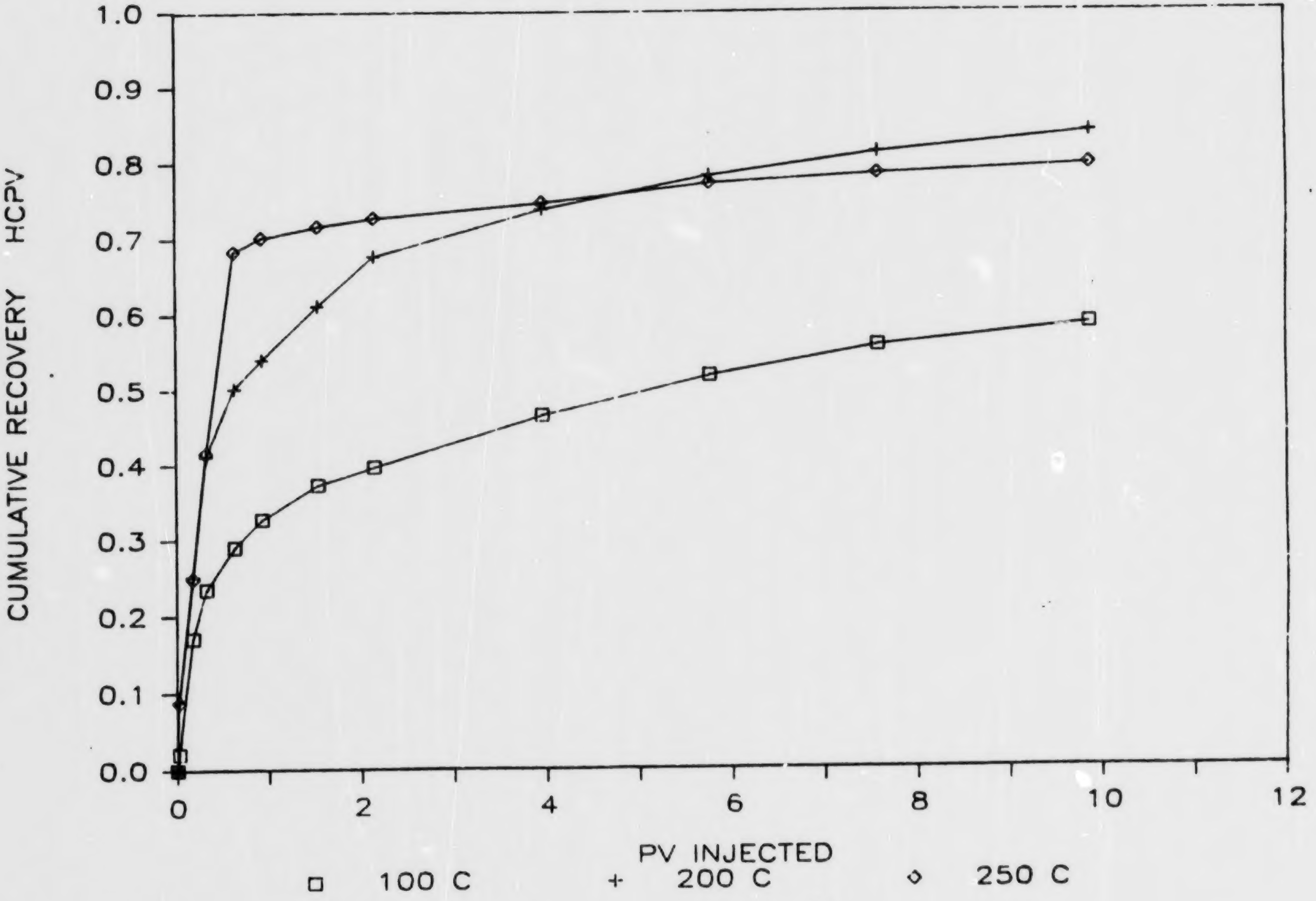
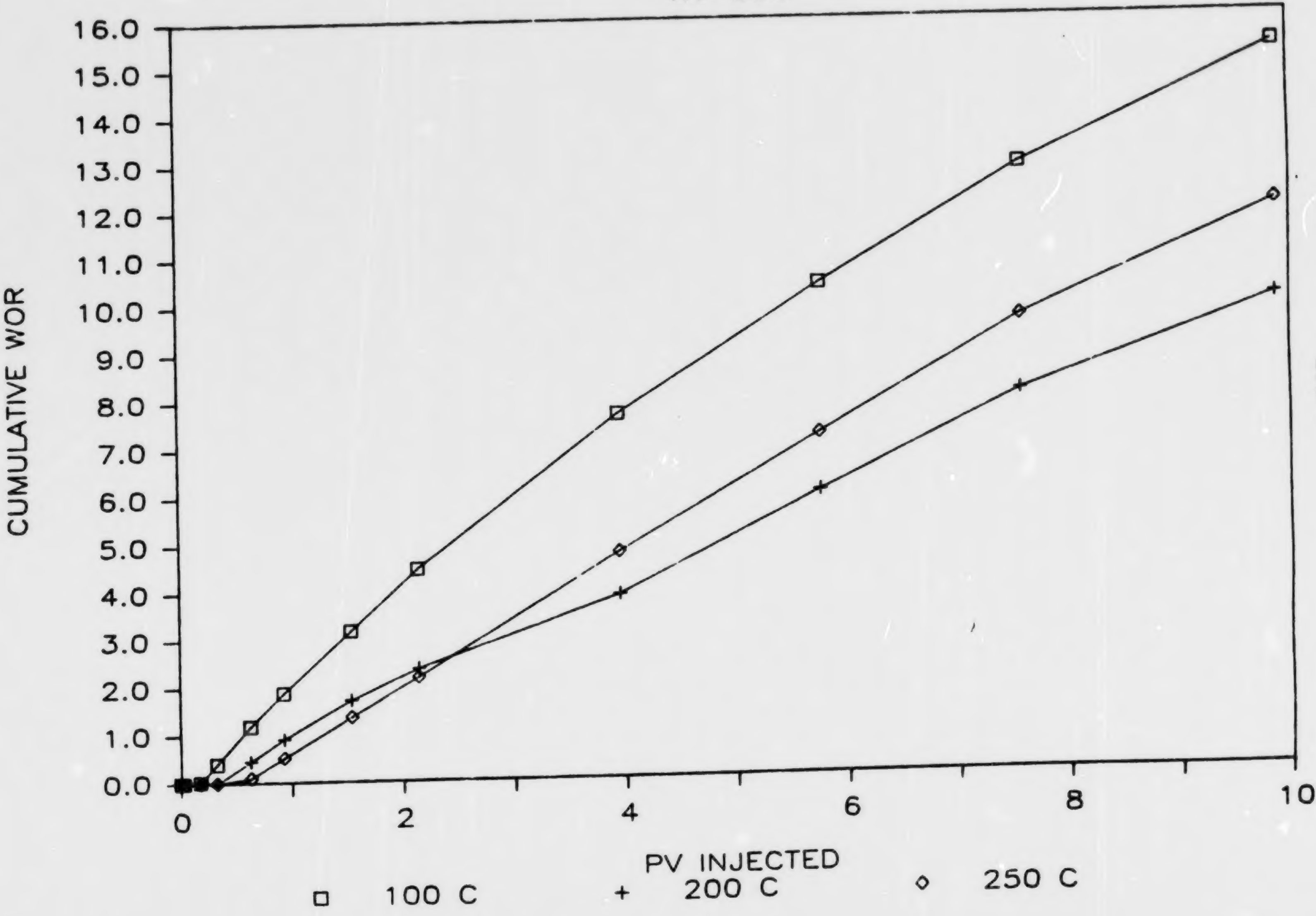


FIGURE 4-31

W.EDAM WATER—OIL RATIO

TH—906



4.4 Statistical Analysis of Displacement Results

A detailed analysis of variance has been carried out to evaluate the statistical significance of the displacement results, Figures 4-2 to 4-23. For each of the two heavy oils, the analysis was based on a Randomized Block design. The type of injection fluid and the operating temperature were the two factors considered in the analysis. According to the experimental scheme, twelve experiments (4 injection fluids, consisting of water and three additive solutions, at three different operating temperatures) were analyzed for each heavy oil. A two factor analysis of variance, on the basis of both the oil recovery and water-oil ratio results, was followed.

To use the method of analysis of variance, interpolation on the oil recovery and water-oil ratio curves was carried out at exactly 4 PV of fluid injection in every case. The analysis of variance was also repeated by considering interpolated results at exactly 6 PV. Repeating the analysis of variance on the basis of oil recovery, water-oil ratio, and at two different points on the recovery curves (4 PV and 6 PV injection) was decided in order to check the consistency of the data and accuracy of interpolations. For each of the two oils, therefore, four analysis of variance tables were developed. The analysis of variance for the West Edam oil is given in Tables 4-1 to 4-4, and that of the Pelican Lake oil is given in Tables 4-5 to 4-8.

TABLE 4-1

```
                  W. EDAM OIL RECOVERY RESULTS (@ 4 PV)
                  *************************************
ANOVA TABLE
-----------
                         TEMPERATURE                        ADDITIVE
FLUID                100 C    200 C    250 C              SUM  AVERAGE

TH-906                0.46     0.75     0.75             1.96 0.653333
TCH-956               0.51     0.67     0.74             1.92     0.64
TRS-410               0.62     0.72     0.76              2.1      0.7
WATER                  0.5     0.68     0.75             1.93 0.643333
                    ------   ------   ------           ------
TEMP SUM              2.09     2.82        3  G. SUM     7.91     7.91
TEMP AVE            0.5225    0.705     0.75         0.659166

                                        CORREC = 5.214008
                                        SS tot = 0.134491
ANOVA SUMMARY
-------------
SOURCE OF VARIANCE
                                df            SUM SQRS           MEAN SQR
BETWEEN TEMPERATURES             2            0.116116           0.058058
BETWEEN ADDITIVES                3            0.006958           0.002319
ERROR                            6            0.011416           0.001902

F-TESTS
-------
BETN TEMPS          30.51240          F CRIT (2/6) =       5.14      SIG.
BETN ADDS           1.218978          F CRIT (3/6) =       4.76  NOT SIG.
```

TABLE 4-2

W. EDAM OIL RECOVERY RESULTS (@ 6 PV)

```
*************************************

ANOVA TABLE
-----------
                           TEMPERATURE                     ADDITIVE
FLUID                100 C    200 C    250 C              SUM  AVERAGE

TH-906                0.53      0.79     0.77              2.09 0.696666
TCH-956               0.57      0.74     0.77              2.08 0.693333
TRS-410               0.71      0.79     0.83              2.33 0.776666
WATER                 0.57      0.73     0.78              2.08 0.693333
                     ------   ------   ------            ------
TEMP SUM              2.38      3.05     3.15  G. SUM      8.58     8.58
TEMP AVE             0.595   0.7625   0.7875             0.715

                                             CORREC =   6.1347
                                             SS tot =   0.1119
ANOVA SUMMARY
-------------
SOURCE OF VARIANCE
                                 df          SUM SQRS          MEAN SQR
BETWEEN TEMPERATURES              2           0.08765          0.043825
BETWEEN ADDITIVES                 3          0.015233          0.005077
ERROR                             6          0.009016          0.001502

F-TESTS
-------
BETN TEMPS        29.16266          F CRIT (2/6) =        5.14      SIG.
BETN ADDS         3.378927          F CRIT (3/6) =        4.76 NOT SIG.
```

TABLE 4-3

```
                      W. EDAM W.O.R. RESULTS (@ 4 PV)
                      ****************************************

ANOVA TABLE
-----------
                           TEMPERATURE                              ADDITIVE
FLUID                100 C      200 C      250 C                 SUM  AVERAGE

TH-906                 7.8          5        4.8                17.6 5.866666
TCH-956                  7        5.7        4.8                17.5 5.833333
TRS-410                5.7        4.6        4.5                14.8 4.933333
WATER                    7        5.8        4.6                17.4      5.8
                    ------     ------     ------              ------
TEMP SUM              27.5       21.1       18.7   G. SUM       67.3     67.3
TEMP AVE             6.875      5.275      4.675          5.608333

                                                  CORREC = 377.4408
                                                  SS tot = 13.66916
ANOVA SUMMARY
-------------
SOURCE OF VARIANCE
                                       df         SUM SQRS               MEAN SQR
BETWEEN TEMPERATURES                    2         10.34666               5.173333
BETWEEN ADDITIVES                       3         1.829166               0.609722
ERROR                                   6         1.493333               0.248888




F-TESTS
-------
BETN TEMPS           20.78571       F CRIT (2/6) =          5.14     SIG.
BETN ADDS            2.449776       F CRIT (3/6) =          4.76 NOT SIG.
```

TABLE 4-4

W. EDAM W.O.R. RESULTS (@ 6 PV)
****

```
ANOVA TABLE
-----------
                          TEMPERATURE                        ADDITIVE
FLUID                100 C     200 C     250 C              SUM  AVERAGE

TH-906                11.1       7.3       7.4              25.8      8.6
TCH-956                9.9         8       7.5              25.4 8.466666
TRS-410                  8         7       6.8              21.8 7.266666
WATER                   10       8.3       7.2              25.5      8.5
                    ------    ------    ------            ------
TEMP SUM                39      30.6      28.9   G. SUM     98.5     98.5
TEMP AVE              9.75      7.65     7.225          8.208333

                                              CORREC = 808.5208
                                              SS tot = 20.96916
ANOVA SUMMARY
-------------
SOURCE OF VARIANCE
                                 df           SUM SQRS           MEAN SQR
BETWEEN TEMPERATURES              2           14.62166           7.310833
BETWEEN ADDITIVES                 3           3.575833           1.191944
ERROR                             6           2.771666           0.461944

F-TESTS
-------
BETN TEMPS          15.82621        F CRIT (2/6) =        5.14       SIG.
BETN ADDS           2.580276        F CRIT (3/6) =        4.76   NOT SIG.
```

TABLE 4-5

```
PELICAN OIL RECOVERY RESULTS (@ 4 PV)
*****************************************

ANOVA TABLE
-----------

                           TEMPERATURE                    ADDITIVE
FLUID               100 C     200 C     250 C            SUM  AVERAGE

TH-906               0.71      0.82      0.72            2.25     0.75
TCH-956               0.7      0.78      0.75            2.23 0.743333
TRS-410              0.67       0.7      0.75            2.12 0.706666
WATER                0.66      0.71      0.69            2.06 0.686666
                   ------    ------    ------          ------
TEMP SUM             2.74      3.01      2.91  G. SUM    8.66     8.66
TEMP AVE            0.685    0.7525    0.7275        0.721666

                                       CORREC = 6.249633
                                       SS tot = 0.023366
ANOVA SUMMARY
-------------
SOURCE OF VARIANCE
                              df          SUM SQRS        MEAN SQR
BETWEEN TEMPERATURES           2          0.009316        0.004658
BETWEEN ADDITIVES              3          0.008166        0.002722
ERROR                          6          0.005883        0.000980

F-TESTS
-------
BETN TEMPS          4.750708        F CRIT (2/6) =      5.14 NOT SIG.
BETN ADDS           2.776203        F CRIT (3/6) =      4.76 NOT SIG.
```

TABLE 4-6

PELICAN OIL RECOVERY RESULTS (@ 6 PV)

```
************************************

ANOVA TABLE
-----------
                            TEMPERATURE                         ADDITIVE
FLUID                  100 C     200 C     250 C               SUM  AVERAGE

TH-906                  0.77      0.85      0.75               2.37     0.79
TCH-956                 0.74      0.82      0.77               2.33 0.776666
TRS-410                 0.73      0.75      0.78               2.26 0.753333
WATER                   0.71      0.73      0.71               2.15 0.716666
                      ------    ------    ------              ------
TEMP SUM                2.95      3.15      3.01   G. SUM      9.11     9.11
TEMP AVE              0.7375    0.7875    0.7525           0.759166

                                                   CORREC = 6.916008
                                                   SS tot = 0.019691
ANOVA SUMMARY
-------------
SOURCE OF VARIANCE
                                   df              SUM SQRS           MEAN SQR
BETWEEN TEMPERATURES                2              0.005266           0.002633
BETWEEN ADDITIVES                   3              0.009291           0.003097
ERROR                               6              0.005133           0.000855




F-TESTS
-------
BETN TEMPS             3.077922         F CRIT (2/6) =         5.14 NOT SIG.
BETN ADDS              3.620129         F CRIT (3/6) =         4.76 NOT SIG.
```

TABLE 4-7

PELICAN W.O.R. RESULTS (@ 4 PV)

ANOVA TABLE

FLUID	TEMPERATURE 100 C	200 C	250 C		ADDITIVE SUM	AVERAGE
TH-906	5	4.4	4.9		14.3	4.766666
TCH-956	5	4.5	4.8		14.3	4.766666
TRS-410	5.2	5	4.9		15.1	5.033333
WATER	5.4	5	5.2		15.6	5.2
	-----	-----	-----		------	
TEMP SUM	20.6	18.9	19.8	G. SUM	59.3	59.3
TEMP AVE	5.15	4.725	4.95		4.941666	

CORREC = 293.0408

SS tot = 0.869166

ANOVA SUMMARY

SOURCE OF VARIANCE	df	SUM SQRS	MEAN SQR
BETWEEN TEMPERATURES	2	0.361666	0.180833
BETWEEN ADDITIVES	3	0.409166	0.136388
ERROR	6	0.098333	0.016388

F-TESTS

BETN TEMPS	11.03389	F CRIT (2/6) =	5.14	SIG.
BETN ADDS	8.322033	F CRIT (3/6) =	4.76	SIG.

TABLE 4-8

PELICAN W.O.R. RESULTS (@ 6 PV)

ANOVA TABLE

	TEMPERATURE				ADDITIVE	
FLUID	100 C	200 C	250 C		SUM	AVERAGE
TH-906	7.6	7	7.7		22.3	7.433333
TCH-956	7.7	7.1	7.5		22.3	7.433333
TRS-410	7.8	7.6	7.6		23	7.666666
WATER	8.1	7.9	8.2		24.2	8.066666
TEMP SUM	31.2	29.6	31	G. SUM	91.8	91.8
TEMP AVE	7.8	7.4	7.75		7.65	
				CORREC =	702.27	
				SS tot =	1.35	

ANOVA SUMMARY

SOURCE OF VARIANCE	df	SUM SQRS	MEAN SQR
BETWEEN TEMPERATURES	2	0.38	0.19
BETWEEN ADDITIVES	3	0.803333	0.267777
ERROR	6	0.166666	0.027777

F-TESTS

BETN TEMPS	6.84	F CRIT (2/6) =	5.14	SIG.
BETN ADDS	9.64	F CRIT (3/6) =	4.76	SIG.

Each table contains the data as interpolated from the recovery or water-oil ratio curve, at the pre-decided injection point of 4 or 6 PV, for each injection fluid and operating temperature. The rest of each table contains standard analysis of variance calculations, showing the sum of squares, correction factor, degrees of freedom, sum and mean squares. At the bottom of each table is a summary of the F-tests, including the critical F-values (at the 95% level) obtained from statistical tables at the specified degrees of freedom.

For the W. Edam oil, it is clear that the analysis of variance, in every case, supports the observation that the effect of temperature on oil displacement is significant. The analysis of variance based on the oil recovery and on WOR results shows that the difference between the four injection fluids, on the other hand, is not statistically significant. The only injection fluid which consistently outperformed water injection was the TRS-410 solution. This is clear in the recovery and water oil ratio results at the 4 PV and 6 PV injection points (Tables 4-1 to 4-4).

For the Pelican Lake oil, both the effects of temperature and additive type, as reflected on the oil recovery results, appear to be statistically insignificant. However, on the basis of the water-oil ratio data, both effects are determined to be statistically significant. This result is not totally surprising; for it reflects the observation that the effects of additives and of temperature in increasing oil recovery and lowering WOR are small. Secondly, interpolation on the highly non-linear recovery curves is less sensitive to the influence of these factors than the WOR curves. From a strictly numerical point of view, interpolation on the largely linear water-oil ratio curves is obviously much more accurate.

4.5 Effect of Additive Concentration

Based on the results of the displacement and permeability experiments, TRS-410 and Thermoflood-906 were selected for further testing with the W. Edam and Pelican Lake oils respectively. The objective of these additional tests was to assess the effect of concentration, of each additive, on the recovery of the respective oils. All the experiments were carried out at a temperature of 200°C. The concentrations of the TRS-410 solutions, used to displace W. Edam oil, were 3000, 4500 and 6000 ppm. The concentrations of the Thermoflood 906, used to displace the Pelican oil, were 200, 400 and 600 ppm.

The results of these experiments are given in terms of oil recovery and water-oil ratio in Figures 4-32 to 4-35. It is clear that the additive concentration has no significant effect, in improving the recovery of either of the two oils. In fact applying the thin film spreading agent Thermoflood 906 at the high concentration of 600 ppm appears to have a small adverse effect on the displacement of the Pelican Lake oil. This could possibly be due to a permeability reduction accompanying the high additive concentration.

4.6 Role of Clay Stabilizers in Oil Displacement

The results of a series of comparative displacement tests, carried out with synthetic cores containing 5% clay homogeneously mixed with Ottawa sand, are given in Figures 4-36 to 4-38. The clay mixture consisted of equal amounts of bentonite and illite, i.e. each at 2.5% of the total weight of the core packing. Each

FIGURE 4-32

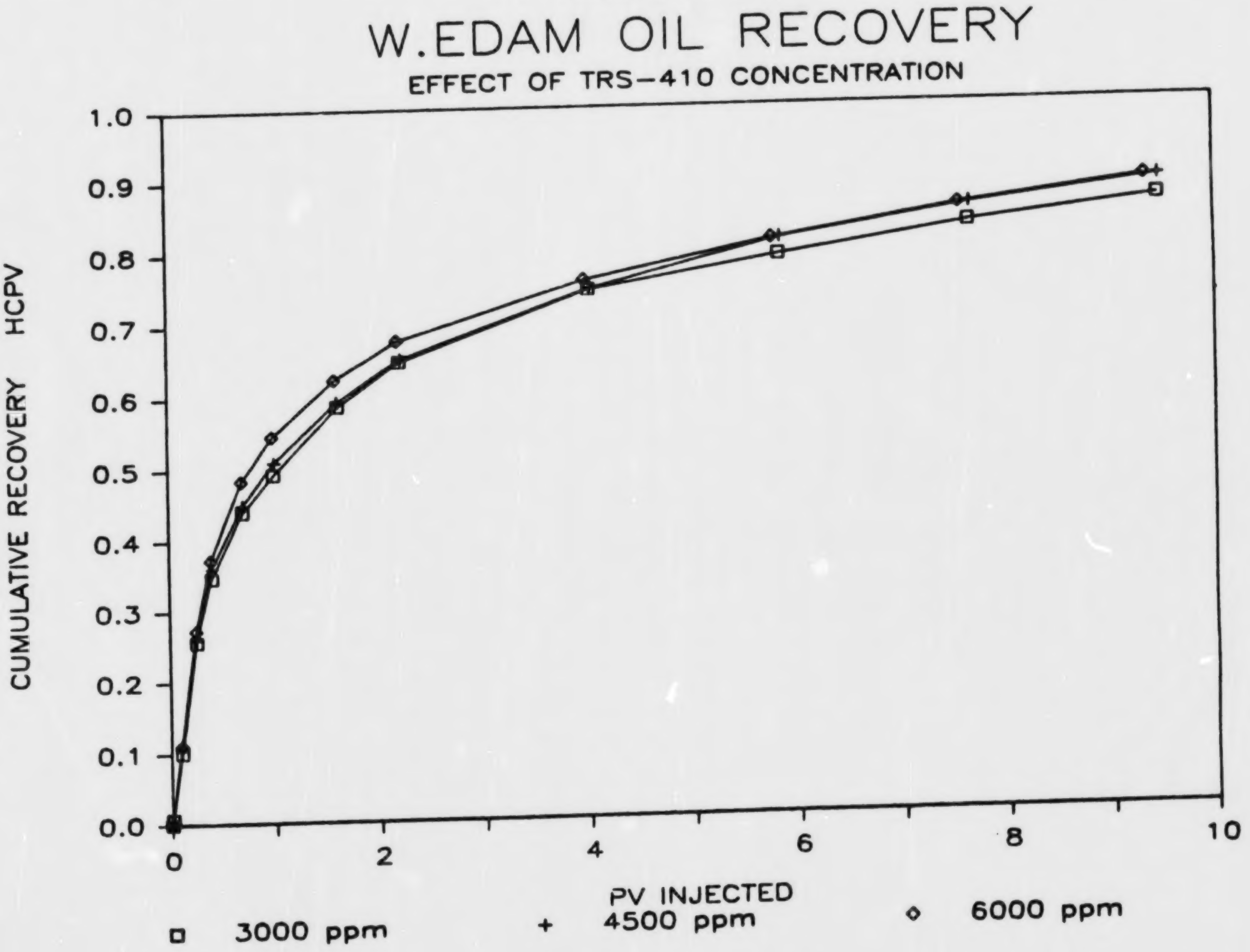

W.EDAM OIL RECOVERY
EFFECT OF TRS-410 CONCENTRATION
CUMULATIVE RECOVERY HCPV
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
PV INJECTED
□ 3000 ppm
+ 4500 ppm
◇ 6000 ppm

FIGURE 4-33

W.EDAM WATER—OIL RATIO

EFFECT OF TRS—410 CONCENTRATION

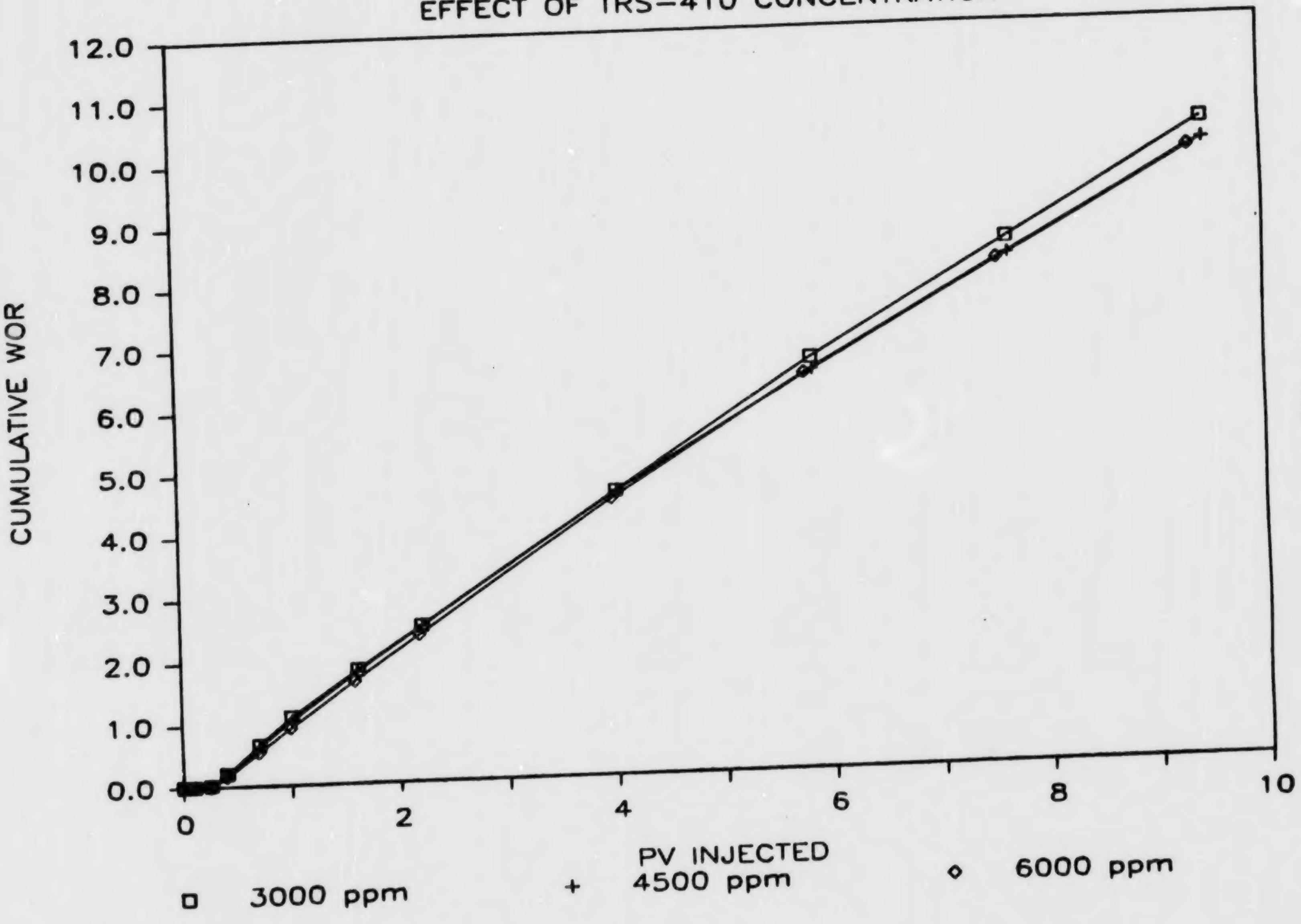


FIGURE 4-34

PELICAN OIL RECOVERY

EFFECT OF TH-906 CONCENTRATION

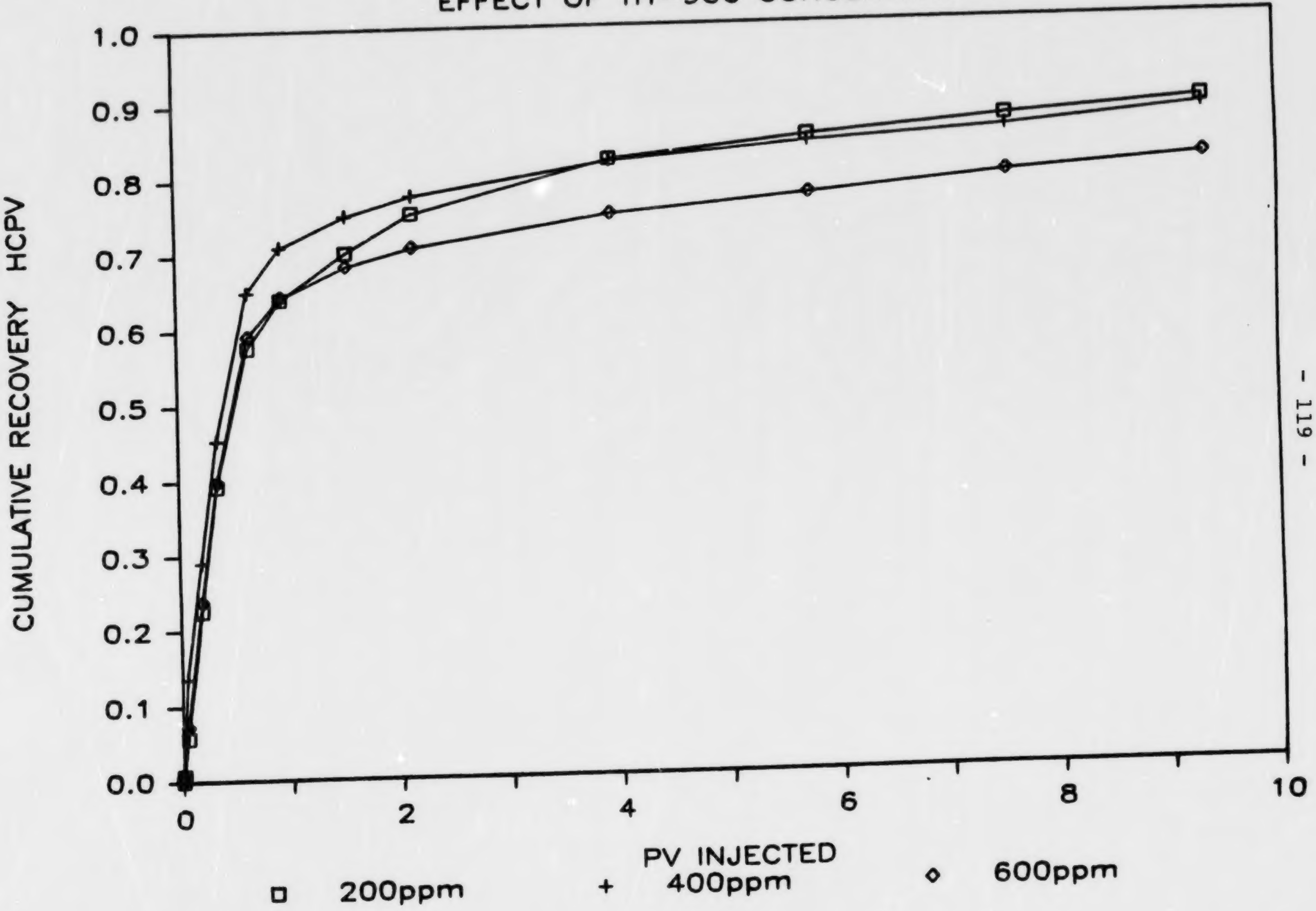
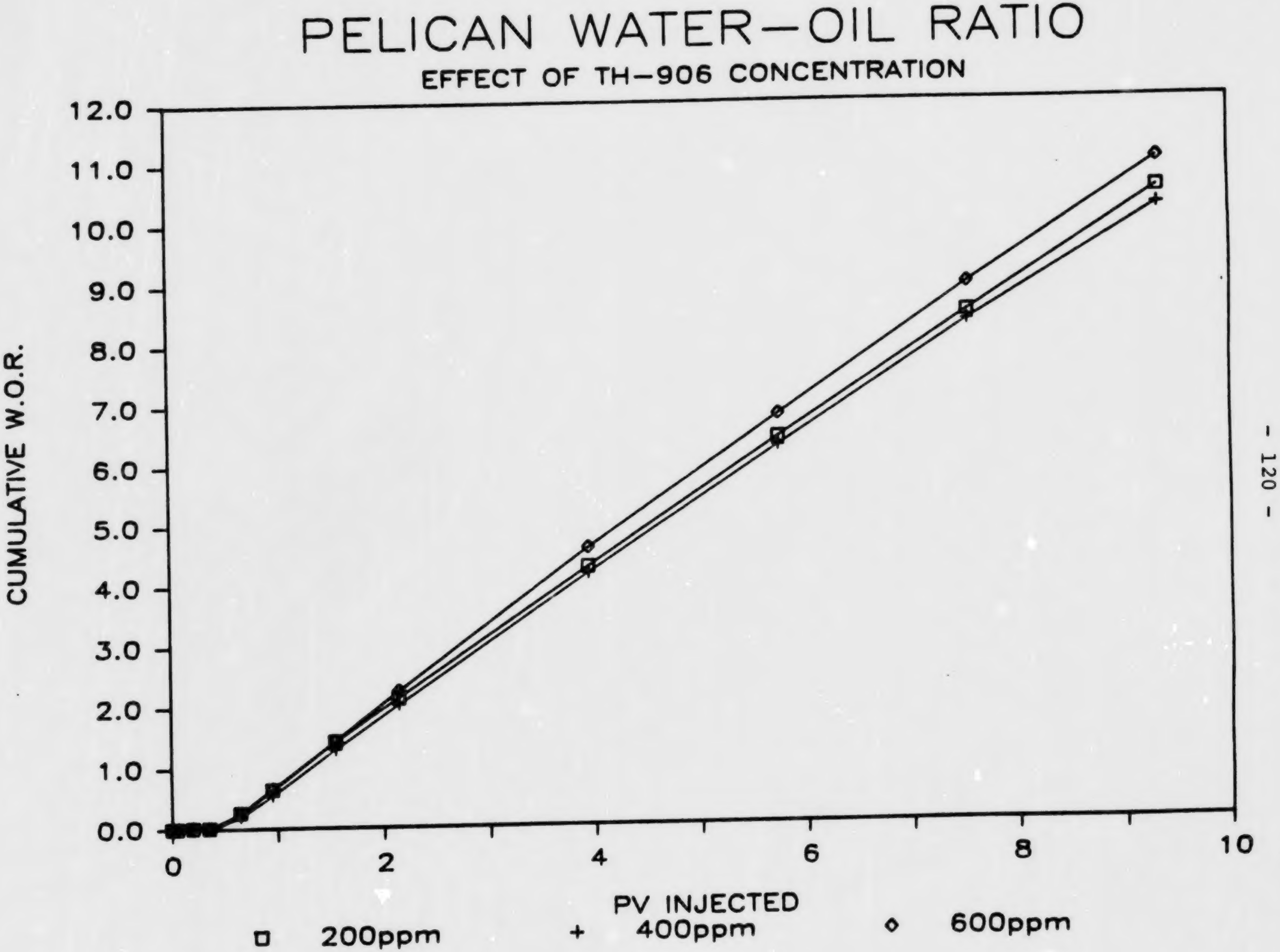


FIGURE 4-35



PELICAN WATER—OIL RATIO

EFFECT OF TH—906 CONCENTRATION

FIGURE 4-36

EFFECT OF CLAY STABILIZERS

ON CUMULATIVE OIL RECOVERY (HCPV)

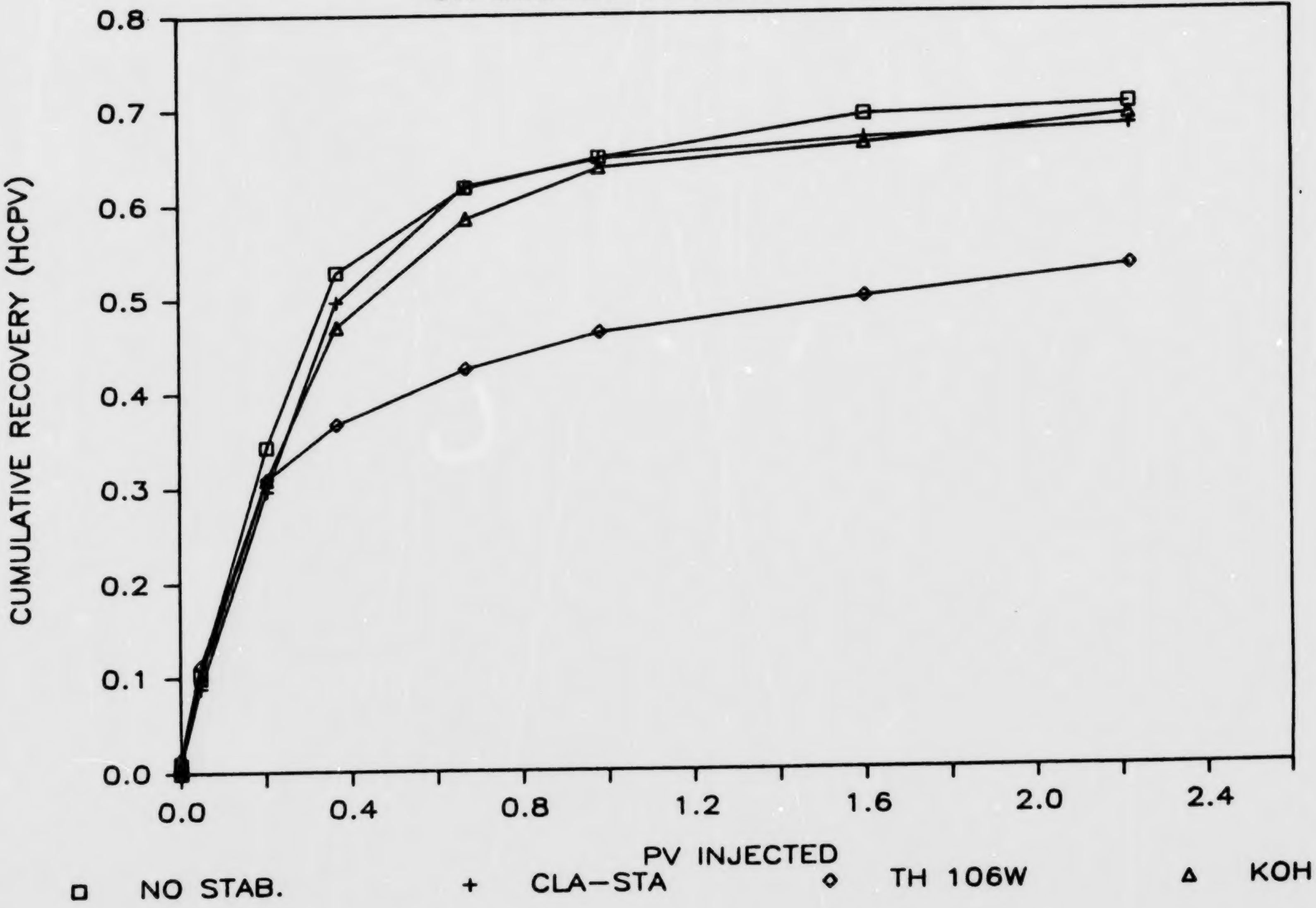


FIGURE 4-37

EFFECT OF CLAY STABILIZERS

ON CUMULATIVE WOR

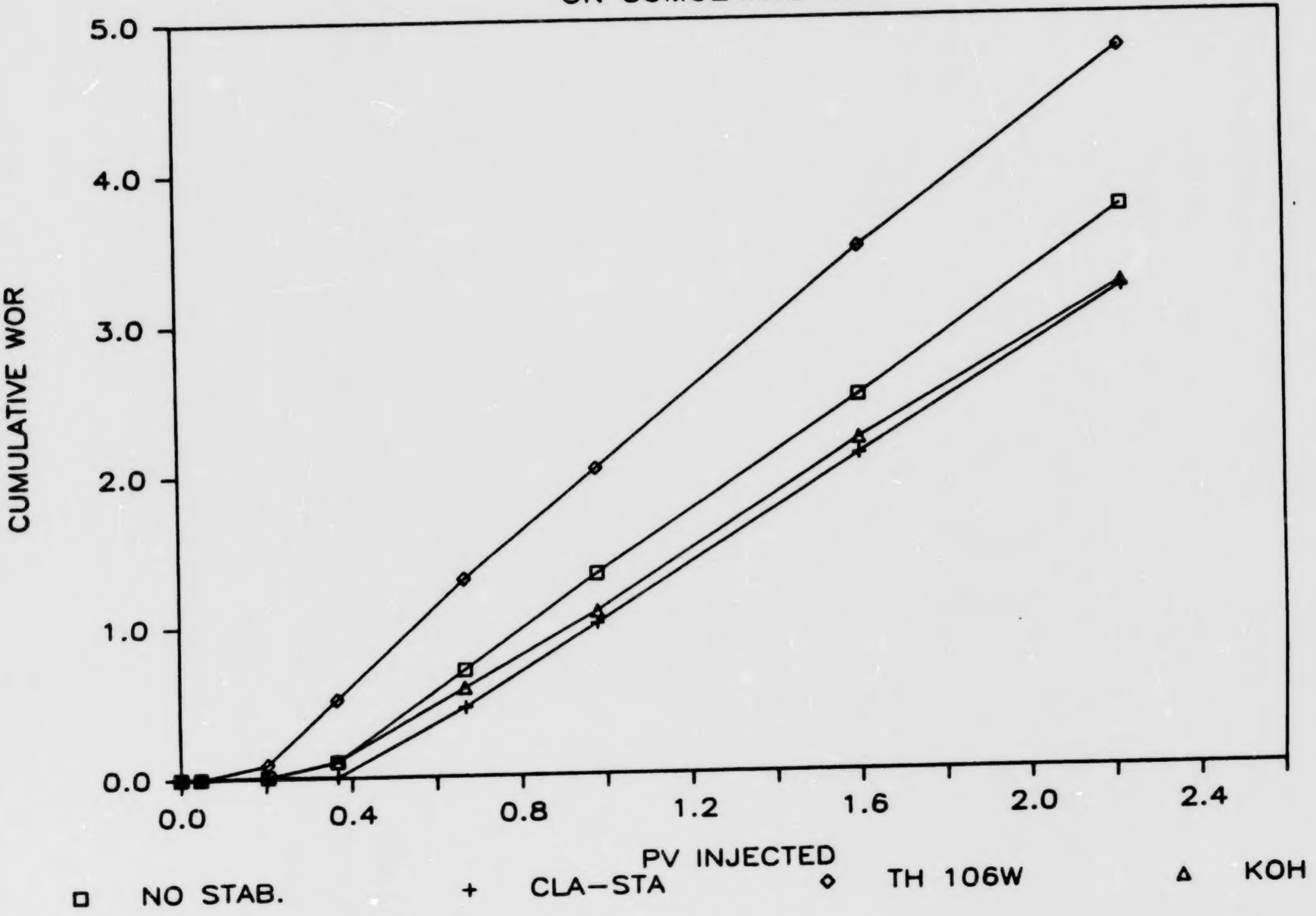
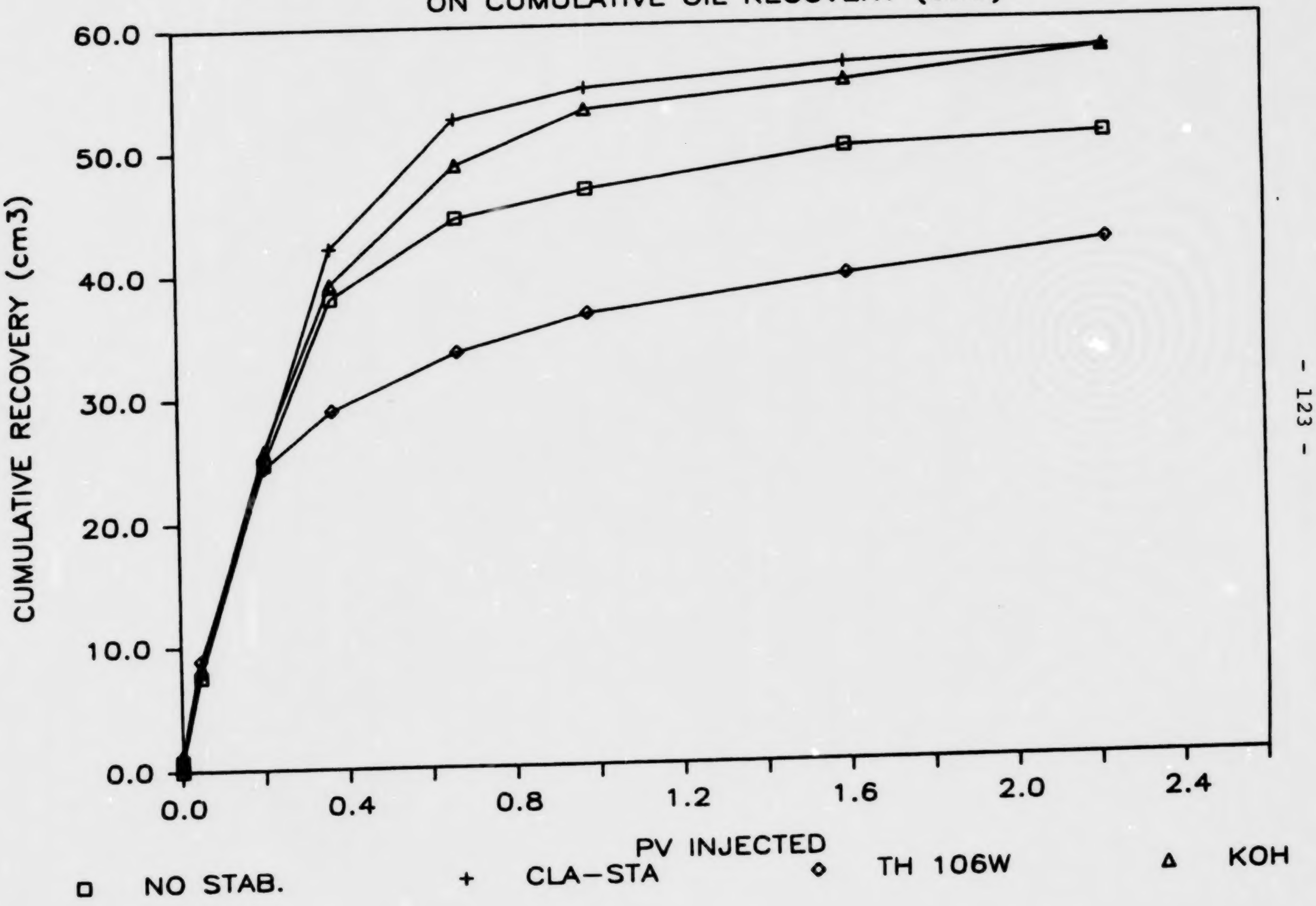


FIGURE 4-38

EFFECT OF CLAY STABILIZERS
ON CUMULATIVE OIL RECOVERY (CM3)



of the clay stabilizers (CLA-STA FS, Thermoflo 106W, and KOH) was used, at its preselected concentration (Table 2-13), to treat the packed core. This was done by first flooding a fresh core with several pore volumes of the clay stabilizer solution. The stabilizer solution was then displaced, with Pelican Lake oil, down to its irreducible level. A reference run with the clay/sand mixture, but no clay stabilizer, was also carried out. In all four displacement experiments, 200 ppm Thermoflood 906 solution was used as the injection fluid to displace the Pelican Lake oil.

Before discussing the results of Figures 4-36 to 4-38, it is important to point out that the oil saturation observed, after additive treatment of the core, showed significant variation between the four runs. For the CLA-STA FS run, the oil saturation HCPV was 80.4%. For the KOH, Thermoflo 106W, and brine solution, HCPV's were 79.1%, 74.6% and 67.8% respectively. These oil saturations are considerably lower than the case of sand cores (no clay present), where HCPV was consistently around 94%. Obviously the presence of the clay mixture results in a significant absorption of water by the core.

The above oil saturations indicate that CLA-STA FS, followed closely by KOH, have a favourable effect on water retention by the clays. This is an important function of clay stabilizers, which may be indicative of increased injectivity in the field. Without the clay stabilizer treatment, the water retention amounts to over 30% of the pore space of the core. In the field, such water retention amounts to very pronounced clay swelling and impaired injectivity.

Figure 4-36 displays the cumulative oil recovery (HCPV) as a function injected pore volumes of Thermoflood 906 solution. It is clear that treatment with Thermoflo 106W had an adverse effect on oil recovery. This may be due to a permeability damage of the core. This suggestion is supported by the observed adverse effect of Thermoflo 106W on the permeability of preserved cores (Section 2). Other recovery curves in Figures 4-36 show nearly identical characteristics. Figure 4-37 which displays the recovery trends in terms of water-oil ratios confirms the above observations. The reference experiment (no clay stabilizer), however, shows higher water-oil ratios than CLA-STA FS or KOH. As mentioned earlier, the water-oil ratio curves usually give a more sensitive representation of the displacements.

To further highlight the comparison between the runs, Figure 4-38 has been prepared to give the cumulative amount of oil recovered (mL) as a function of fluid injection. Thus, while Figure 4-36 essentially normalizes the results in terms of HCPV, Figure 4-38 shows absolute amounts of recovered oil. It is clear that, even in this presentation of data, Thermoflo 106W shows an adverse effect on the displacement.

It is finally interesting to compare the displacement data of Figure 4-36 with the earlier results (Section 4.2), where no clays were present in the core. The comparison shows generally similar trends. The ultimate recoveries also appear to be comparable in magnitude (in terms of HCPV). The absolute amount of oil recovered, however, is considerably less in the case of clay-sand mixtures; for in this case the initial oil saturation is much lower due to water retention by the clays.

5. INTERFACIAL TENSION STUDY

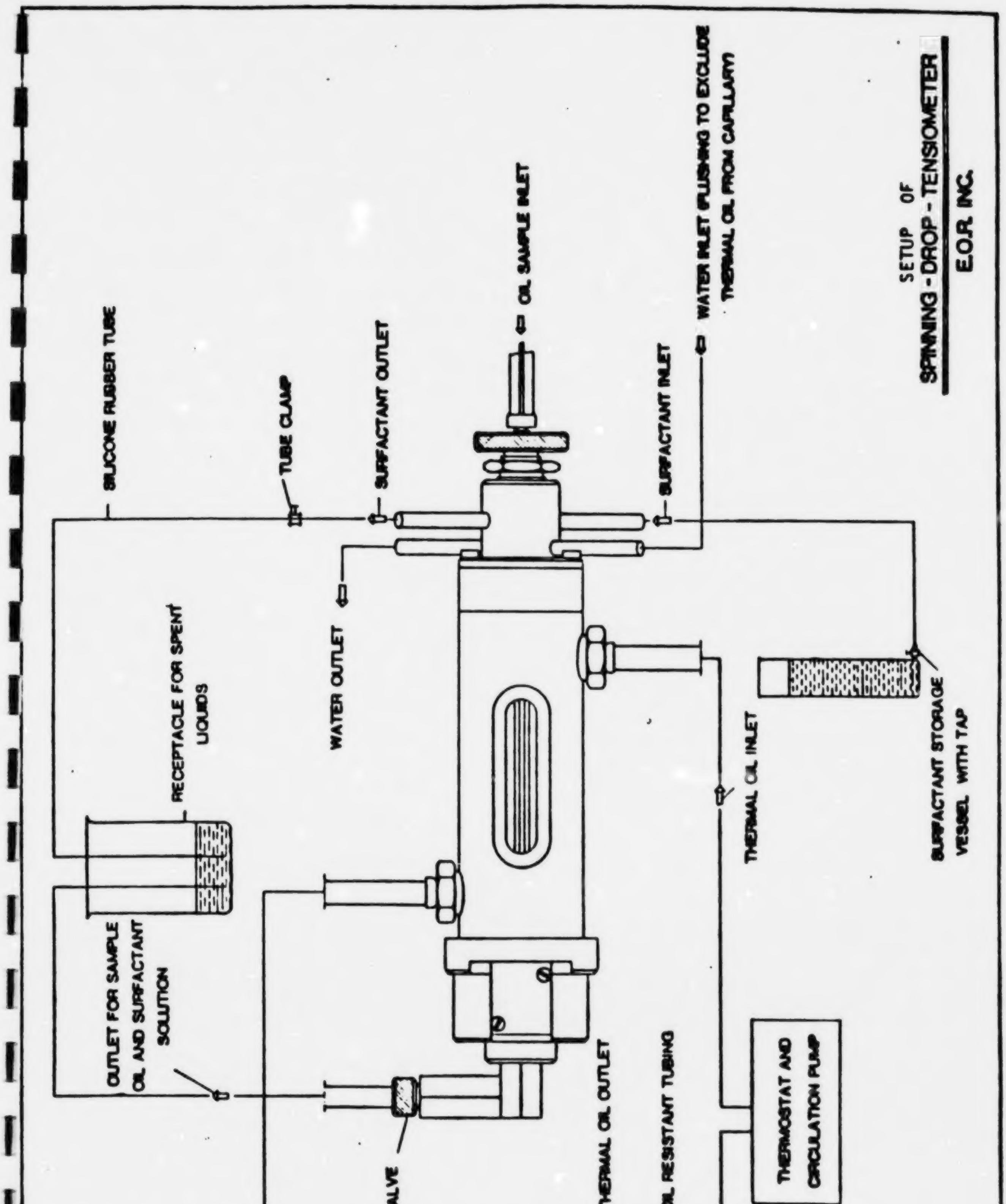
Many of the steam additives, applied to enhance heavy oil recovery, are known to result in varying degrees of interfacial tension reduction. To complement the oil displacement study, and to more fully understand the interfacial tension interactions of each additive, IFT measurements were carried out. In this part of the study, the effect of concentration of each of the three steam additives, on the interfacial tension with the two heavy crudes, is investigated.

5.1 IFT Measurements

All the interfacial tension measurements were carried out using a SITE LP-10 Spinning Drop Interfacial Tensiometer (EOR Inc., Houston, Texas). A description of the instrument and its capabilities has been reported in a number of publications, e.g. (67, 68, 69).

In addition to a connected temperature bath, the instrument consists of four major components: a spinning cell, a tilting base, an electronic control box, and a microscope arrangement. Details of the parts of the instrument will not be given here; but may be found in the instrument operating manual (70). For easy reference, however, the set-up of the SITE LP-10 Spinning Drop Tensiometer is shown in Figure 5-1.

A number of points, specific to the instrument used in this study, are important to mention here:-



SETUP OF
SPINNING - DROP - TENSIOMETER
E.O.R. INC.

SILICONE RUBBER TUBE
TUBE CLAMP
SURFACTANT OUTLET
OIL SAMPLE INLET
SURFACTANT INLET
WATER INLET (FLUSHING TO EXCLUDE THERMAL OIL FROM CAPILLARY)
WATER OUTLET
RECEPTACLE FOR SPENT LIQUIDS
THERMAL OIL INLET
SURFACTANT STORAGE VESSEL WITH TAP
OUTLET FOR SAMPLE OIL AND SURFACTANT SOLUTION
VALVE
THERMAL OIL OUTLET
OIL RESISTANT TUBING
THERMOSTAT AND CIRCULATION PUMP

FIGURE 5-1

- The eyepiece scale, of the microscope arrangement, is only relative and must be calibrated against a true scale. The value obtained may vary slightly from one microscope to another, even for the same standard 63 mm objective lens. We have calibrated our microscope vernier scale against a very accurate optical reticle. A value of 349 vernier scale units/cm was obtained. This value was consistently used in all the IFT calculations.

- Because of light refraction effects, due to the curved surface of the rotating capillary, the drop diameter obtained with the microscope micrometer in vernier scale units is only an "apparent" dimension. The "actual" drop diameter must be obtained from the measured apparent value either using a calibration factor, or via light refraction calculations. The latter approach was used in our calculations by taking into account the refractive indeces of the continuous phase in the rotating tube and the thermal oil surrounding the rotating capillary. The refractive index of the continuous phase was always taken as 1.333 (equal to that of water). The thermal oil used throughout the course of the measurements was Dow Corning "200 Fluid 50 cs" silicone oil, which has a refractive index of 1.4. From these values and for small drop diameters, the actual diameter D was calculated from the apparent diameter D_{app} as:-

$$D = 1.05\ D_{app}$$

For the determination of interfacial tension by the spinning drop method, one must measure the following quantities: the density of the continuous phase, density of the oil phase, rotation speed, the centre diameter of the spinning drop, and length of the spinning drop. The densities of the two phases were independently measured, as given in the characterization section (Sec. 2). The rotation speed was directly provided by the instrument's internal photo-switch/RPM readout arrangement; and was independently checked with a strobe light unit. The dimensions of drop, used for IFT calculations, were measured as a function of time.

After finishing the measurements on a particular system, it was found very important to thoroughly flush and completely clean not only the rotating tube but also the connecting pipe-work. Thus, several hundred mL of the new additive solution were used to flush the entire system. We have also, always, followed the practice of starting out with the lower additive concentration system, then flushing and cleaning with the next higher concentration to be studied.

5.2 Interfacial Tension Results and Discussion

Preliminary IFT measurements on the different combinations of steam additives with Pelican Lake or West Edam heavy oils, indicated that high interfacial tensions may be encountered with a number of these systems. The spinning drop technique is best suited for low interfacial tension systems with large density difference between the two phases. For such systems, the length-to-diameter ratio of the spinning drop, L/D, is greater than 4. For small L/D ratios a shape factor must be introduced in the IFT calculations. Using large shape factors, particularly for L/D ratios below 2, can adversely affect the accuracy of the calculations.

Theoretical values for the spinning drop shape factor, as a function of L/D, are accurately known in the literature (71). However, they may only be found in a discrete tabular form or in a less accurate graphical presentation. Due to the need for repeated application of the shape factors, it was felt necessary to develop accurate algebraic correlations for these purposes. Non-linear regression routines were, thus, used to develop the necessary correlations over three selected ranges of L/D ratios. Dividing the L/D ratios into three separate ranges was necessary to enhance the accuracy of the correlations.

Table 5-1 summarizes the correlations developed for the three L/D ratio ranges. Within each range, the corresponding correlation estimates the shape factor to better than 1.3% of the theoretical value. Figure 5-2 and Table 5-2 illustrates the accuracy of the developed correlations. In Figure 5-2, the solid line represents the correlations, while the points indicate the theoretical shape factors.

Preliminary interfacial tension measurements on spinning drops of Pelican Lake and W. Edam oils in aqueous saline solutions containing the sulfonate additive TRS-410 indicated a significant decrease of IFT with time. It was, therefore, decided to carry out a detailed experimental investigation of this effect for each oil/interfacial additive solution system. The additive concentrations employed ranged from 3000 to 10,000 ppm.

The results of IFT measurements, on Pelican Lake and W. Edam spinning drops, are shown in Figures 5-3 and 5-4. Two main factors may be seen to have pronounced effects on the interfacial tension. These two factors are the age of the spinning oil drop and the age of the additive solution.

TABLE 5-1

SPINNING DROP SHAPE FACTOR CORRELATIONS

* $f(L/D) - 1 = a \left(\frac{L}{D} - 1\right)^{-b} - c$

Correlation	Range	a	b	c
1	$1.002 < L/D \leq 1.05791$	0.5303	0.9905	0.8812
2	$1.05719 < L/D \leq 2.02922$	0.4177	1.0590	0.2629
3	$2.02922 < L/D < 4$	0.14158	0.4558	0.0845

* f (L/D) spinning drop shape factor

  - for L/D > 4, f (L/D) = 1

  - L/D < 1.002, no shape factor correlation defined

TABLE 5-2

COMPARISON OF THEORETICAL AND CORRELATION SHAPE FACTORS OF SPINNING DROPS

Correlation	L/D	Theoretical f (L/D)	Calculated f (L/D)
1	1.002	250	250.07
	1.00685	74.074	73.96
	1.01626	31.25	31.48
	1.03231	16.00	16.01
	1.05719	9.259	9.14
2	1.09409	5.831	5.841
	1.14811	3.906	3.894
	1.22730	2.743	2.743
	1.34862	2.0	2.012
	1.55473	1.503	1.517
	2.02922	1.157	1.142
3	3.00120	1.024	1.022
	3.05998	1.022	1.0204
	3.12695	1.019	1.0188
	3.20307	1.017	1.0172
	3.29164	1.014	1.0154
	3.39559	1.012	1.0134
	3.52485	1.009	1.011
	3.69276	1.007	1.0083
	3.93236	1.0046	1.0048

FIGURE 5-2

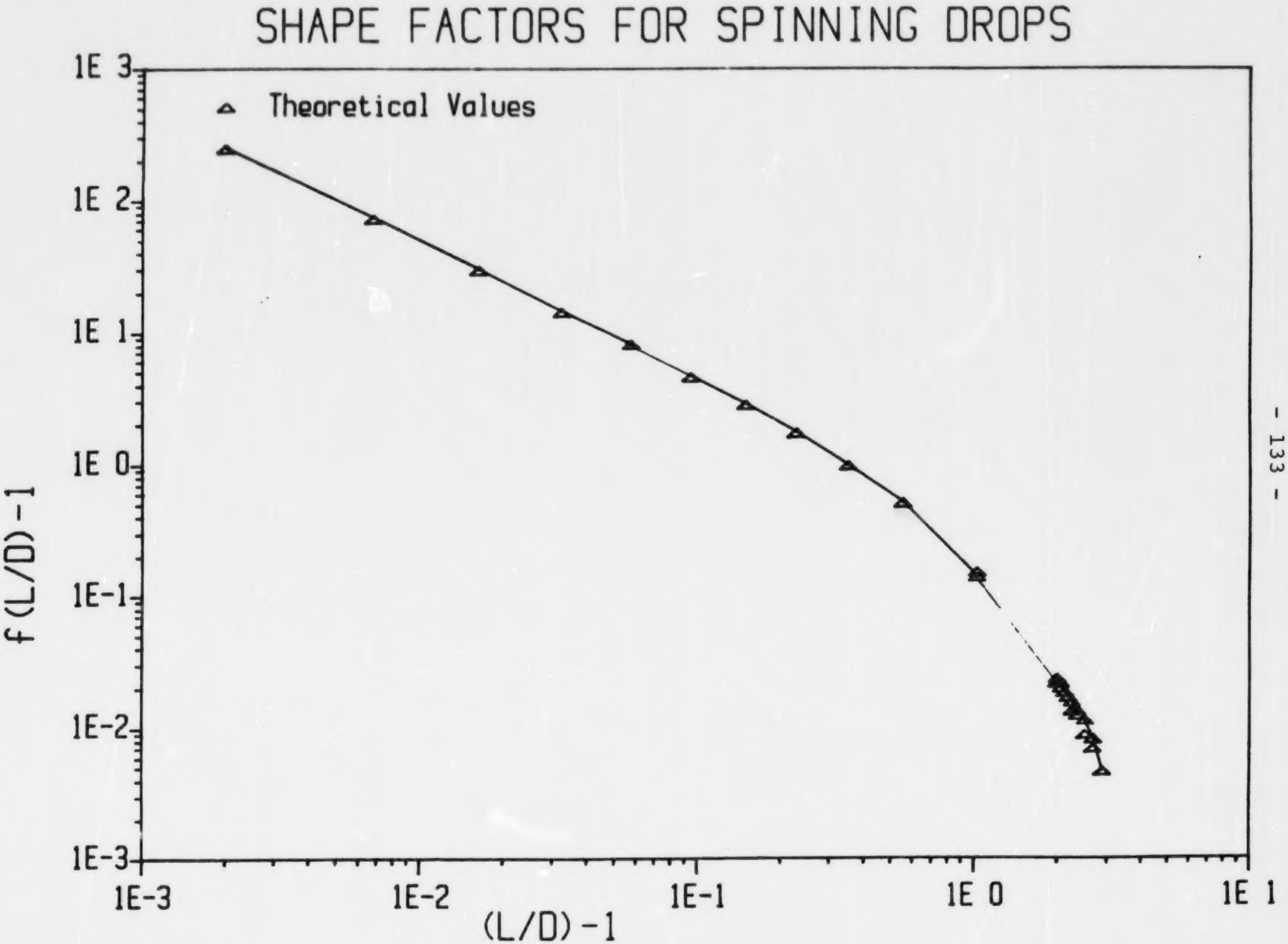
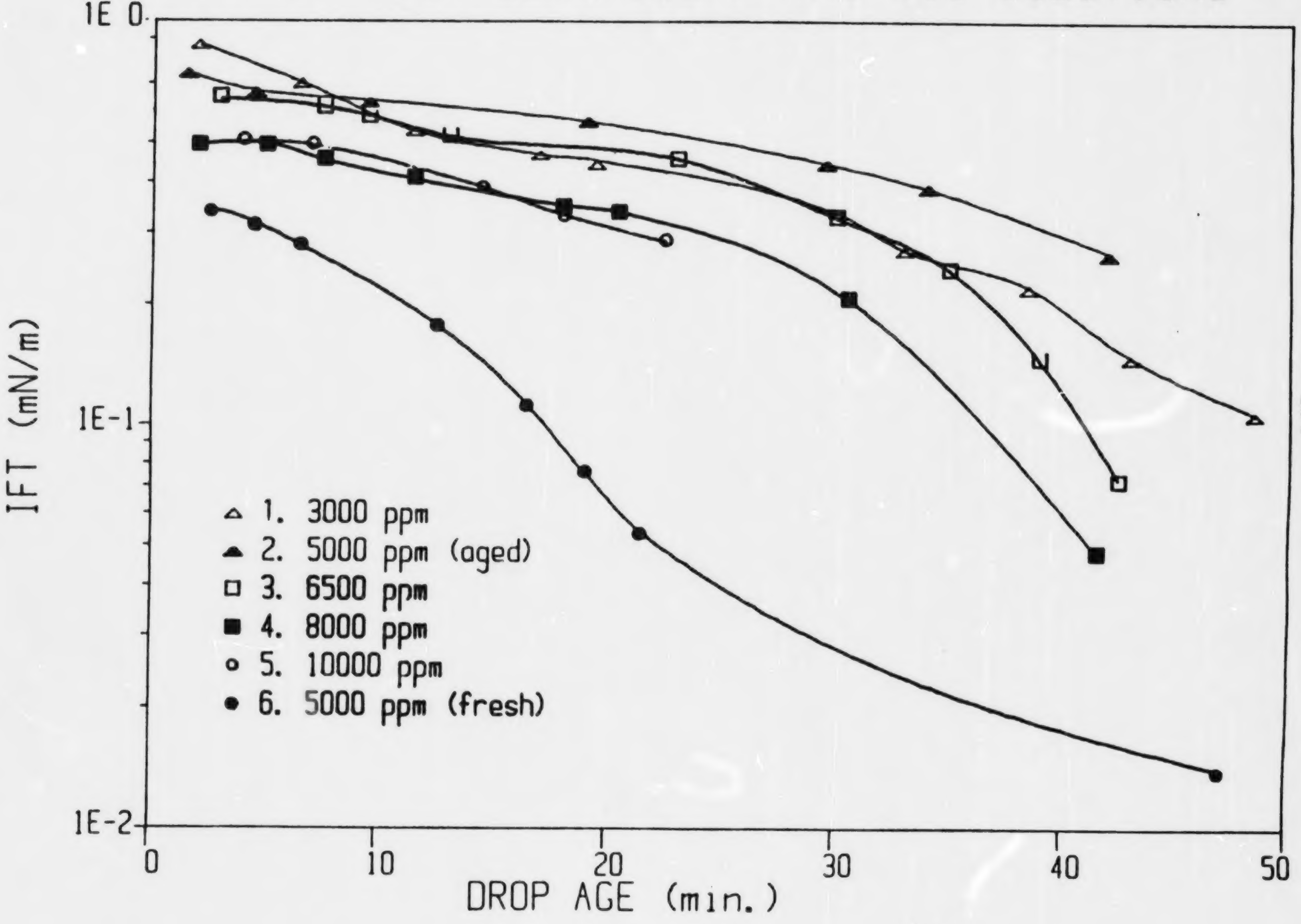

SHAPE FACTORS FOR SPINNING DROPS
Theoretical Values
1E 3
1E 2
1E 1
1E 0
1E-1
1E-2
1E-3
f(L/D)-1
1E-3
1E-2
1E-1
1E 0
1E 1
(L/D)-1

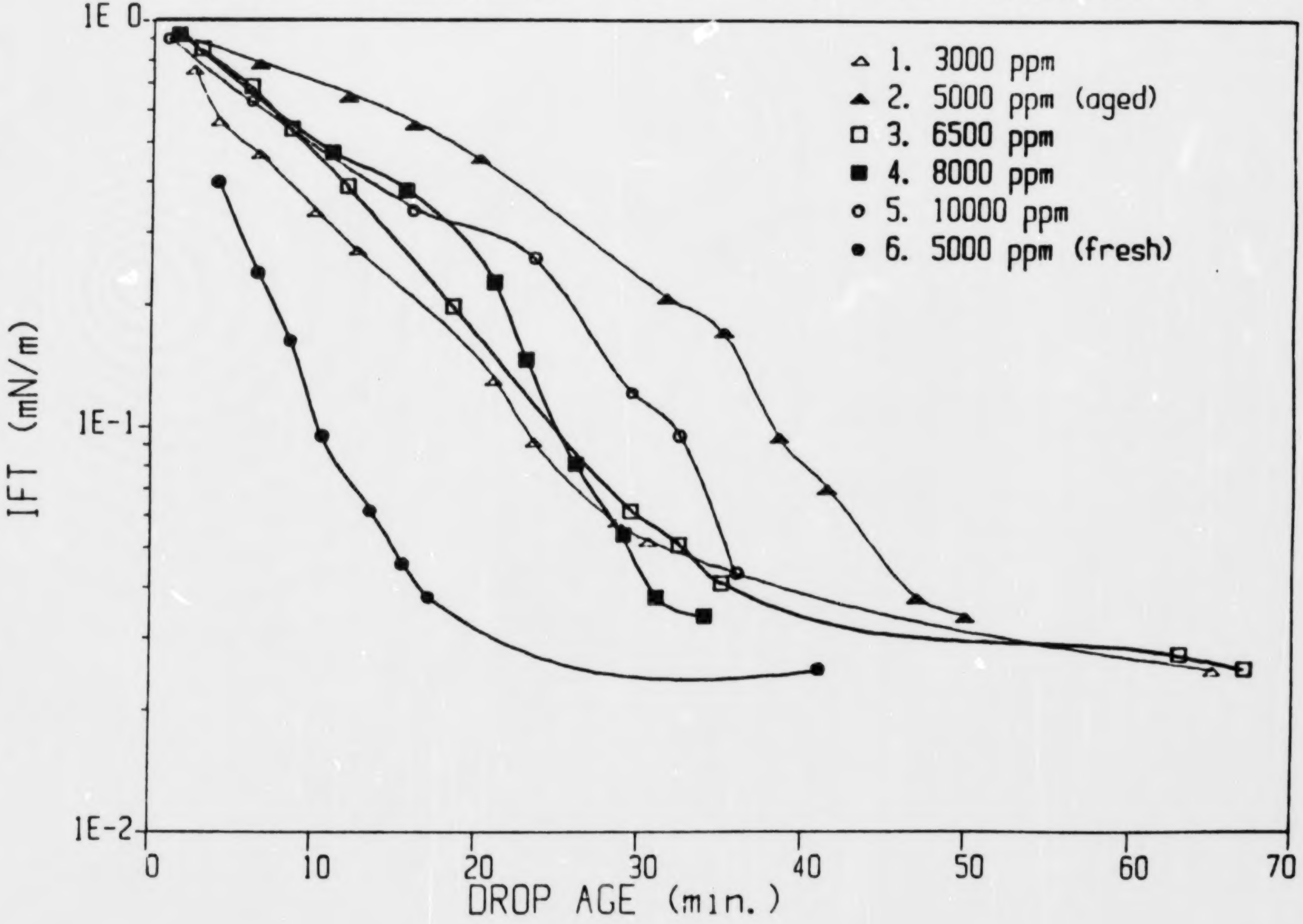
FIGURE 5-3

IFT OF WEST EDAM OIL / TRS 410 SOLUTIONS



F[illegible]RE

IFT OF PELICAN OIL / TRS 410 SOLUTIONS



In the two figures, a significant decrease of IFT with time may be observed for each oil drop/additive solution system studied. In addition to this effect, the freshness of additive solution played a more significant role in determining the interfacial tension. Aging of the additive solution resulted in a pronounced increase in the measured IFT. In the two figures, 5-3 and 5-4, three additive solution conditions are considered. They are:-

- fresh 5000 ppm solution
- 5000 ppm solution aged for several days before applying in spinning drop measurements
- 3000, 6500, 8000 and 10,000 ppm solutions stored for a considerably shorter period of time than the aged 5000 ppm solution (only few hours in the former case, compared to several days in the latter). The four solutions were also prepared using very similar procedure, and were thoroughly shaken before measurements.

The results indicate that, under the same conditions of additive preparation and storage, there is a small tendency of IFT to decrease with increased additive concentration in the case of the W. Edam oil. For the Pelican Lake oil, even this trend is nearly non-existent.

Interfacial tension measurements on Pelican Lake and W. Edam oil drops in aqueous saline solutions containing either the TCH-956 or Thermoflood 906 are given in Tables 5-3 and 5-4. For TCH-956, five concentrations ranging from 25 to 500 ppm have been examined. The Thermoflood-906 concentrations investigated ranged from 200 to 1000 ppm.

TABLE 5-3

INTERFACIAL TENSION OF TCH-956 SOLUTIONS/OIL SYSTEMS

Concentration of TCH-956 (ppm)	IFT (mN/m)	
	W.Edam Oil	Pelican Oil
25	1.26	1.41
50	1.17	1.60
125	1.10	1.61
250	1.07	1.55
500	1.11	1.19

TABLE 5-4

Interfacial Tension of Thermoflood 906 Solutions/Oil Systems

Concentration of Thermoflood 906 (ppm)	IFT mN/m	
	W. Edam Oil	Pelican Oil
200	1.32	1.70
400	1.50	1.42
600	1.40	1.70
800	1.17	1.87
1000	1.37	1.61

As may be observed from the two tables, the interfacial tensions of both the W. Edam and Pelican oils remain largely unaffected by additive concentration. The Pelican oil interfacial tension is generally higher than the W. Edam oil interfacial tension, at the same additive concentration, for both the Thermoflood-906 and TCH-956 systems. Unlike the measurements with the sulfonate additive TRS-410 solutions, no age effects were observed during the course of measurements with THC-956 or Thermoflood-906. In addition, the measurements were not affected by whether the additive solution was freshly prepared or not.

6. EFFECT OF CLAY STABILIZERS ON FLOCCULATION OF PARTICLES

Clay minerals present in petroleum reservoirs are usually found in the flocculated state. Injection of fluids with smaller cation concentration or fluids containing deflocculation ions may lead to the separation of clay particles from each other or from sand grains. Dislodging and dispersion of these particles can result in constriction, or complete plugging, of pore throats. Additives which promote the flocculation of particles would help in maintaining formation permeability and oil productivity.

It was, therefore, found useful to evaluate, and compare, the effectiveness of the three clay stabilizers (CLA STA-FS, Thermoflo 106-W, and KOH) in promoting flocculation. The rate of clay particles settling in an additive solution was considered as a measure of the degree of flocculation. Sludges and suspensions of flocculated particles vary greatly in their settling characteristics, but fast settling rates generally indicate higher degree of flocculation and vice versa. Flocculated particles are also characteized by complex structure of settling flocs and by complex settling mechanisms. In general, however, the settling velocity of a flocculated suspension is constant during the early period of the sedimentation process. As the solid particles accumulate in the bottom zone of the suspension container, the rate of settling decreases steadily until a certain minimum height of particles is reached.

6.1 Settling Experiments

A settling experiment consisted of the following steps:-

1. A specific constant amount (5.0 g) of clay particles were dispersed in 100 mL of additive solution in a graduated cylinder. Identical graduated cylinders were used in all the experiments.

2. The particles were shaken in the additive solution for five minutes.

3. The settling rate was determined immediately after stopping the shaking, by measuring the height (% volume) of the particle suspension zone as a function of time. Alternatively the height of the top clear liquid zone (particle-free zone) could have been measured.

Solutions of four different clay stabilizers were tested in the experiments. These solutions are as follows:-

- CLA-STA FS (1 vol% in 4 wt% KCl)
- Thermoflo 106-W (2000 ppm)
- Potassium hydroxide (15 g/L)
- Potassium chloride (4 g/L)

Each of the above solutions was tested with each of three types of fines. The different clays had approximately the same particle size distributions (71 wt% passing 250 mesh, with the rest of the particles ranging between 170 to 250 mesh). The three clays were:-

- bentonite (a swelling clay)
- illite (a migrating clay)
- Pelican Lake core fines (actual core material)

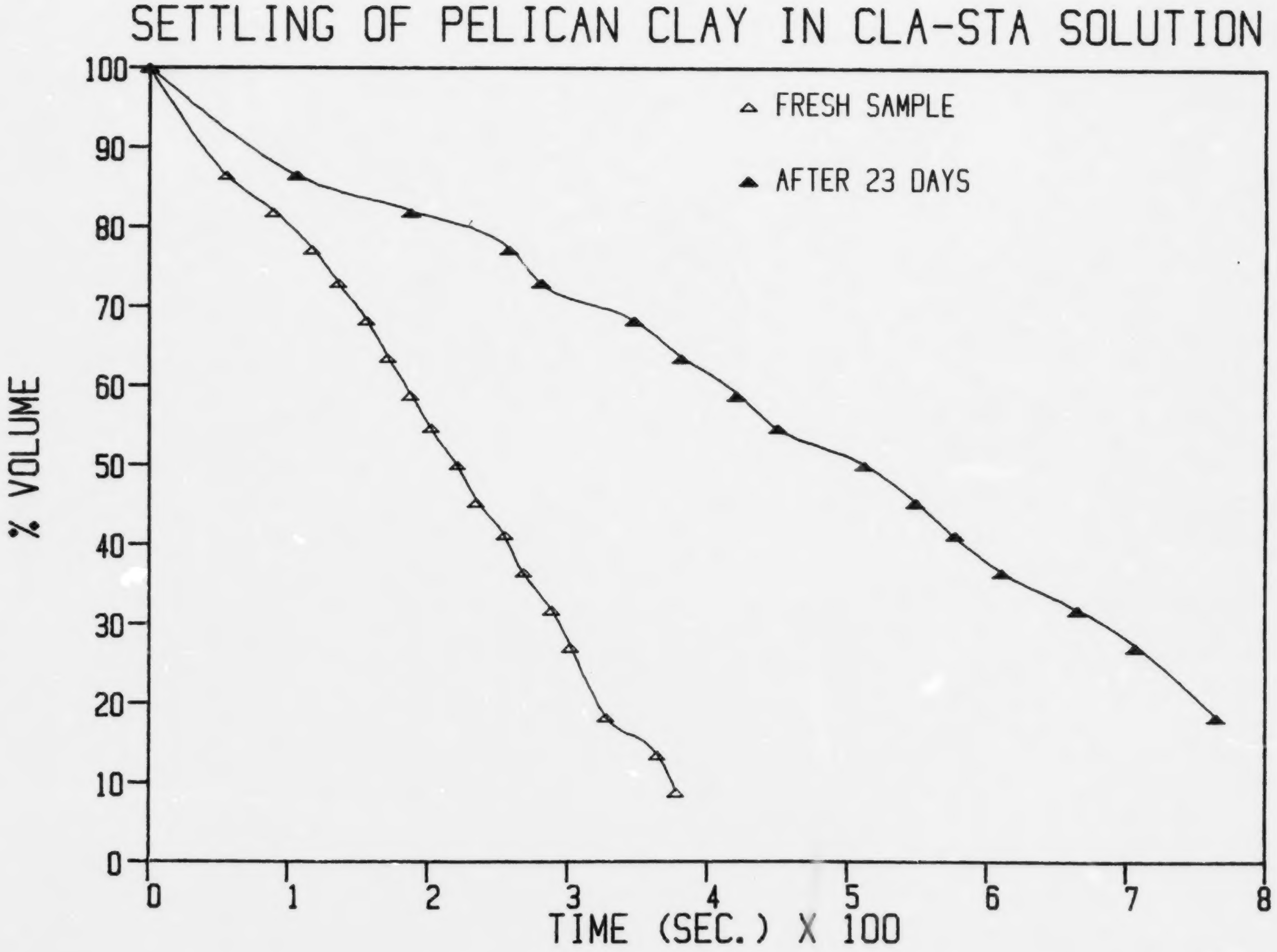
6.2 Settling Experiments Results and Discussion

Figures 6-1 to 6-10 show the characteristic settling curves of the different clay fines in the various clay stabilizing solutions. In addition to the experiments represented in the ten figures, tests were carried out with the three clays in distilled water. Moreover, two experiments with illite and bentonite in Thermoflo 106-W solution were conducted. In each one of the latter five tests, the clay particles remained suspended for extended periods of time. Thus for over one week, in each case, no significant settling could be observed, except for a small fraction of large particles eventually forming a thin bottom layer. In these cases, the solution remained very cloudy, and a significant fraction of the particles was suspended on top of the solution.

The following points highlight the results given in Figures 6-1 to 6-10:-

- For nearly all the clay-additive solution combinations examined, a pronounced age effect was noticable. Each clay-clay stabilizer mixture was, therefore, monitored for a month, and the settling rate was recorded several times during this period. The only exceptions were the cases of bentonite in CLA-STA FS solution and in KCl solution, where little change to the characteristic settling curves occurred due to aging of mixture.

FIGURE 6-1



SETTLING OF PELICAN CLAY IN CLA-STA SOLUTION

FIGURE 6-2

SETTLING OF BENTONITE IN CLA-STA SOLUTION

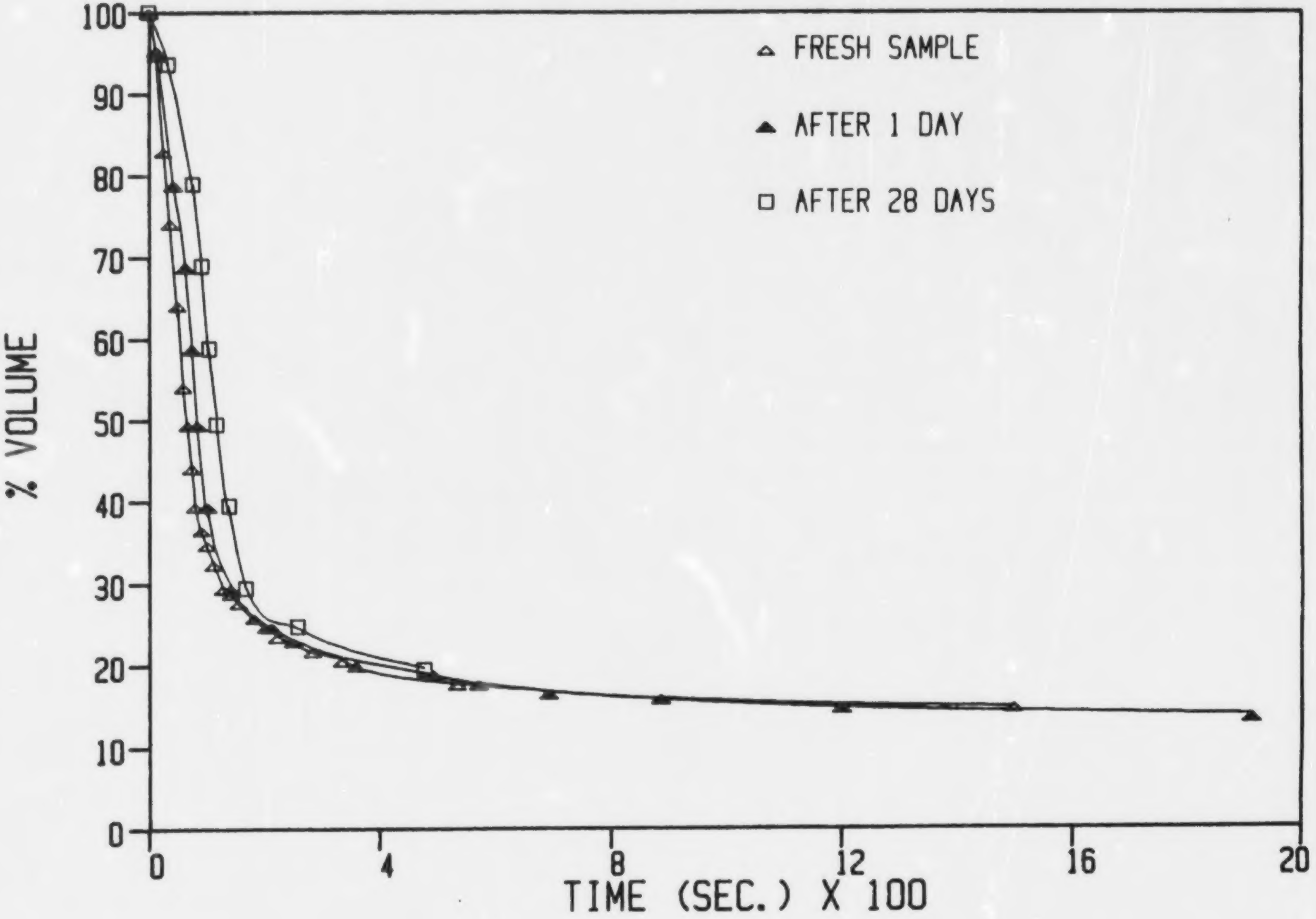
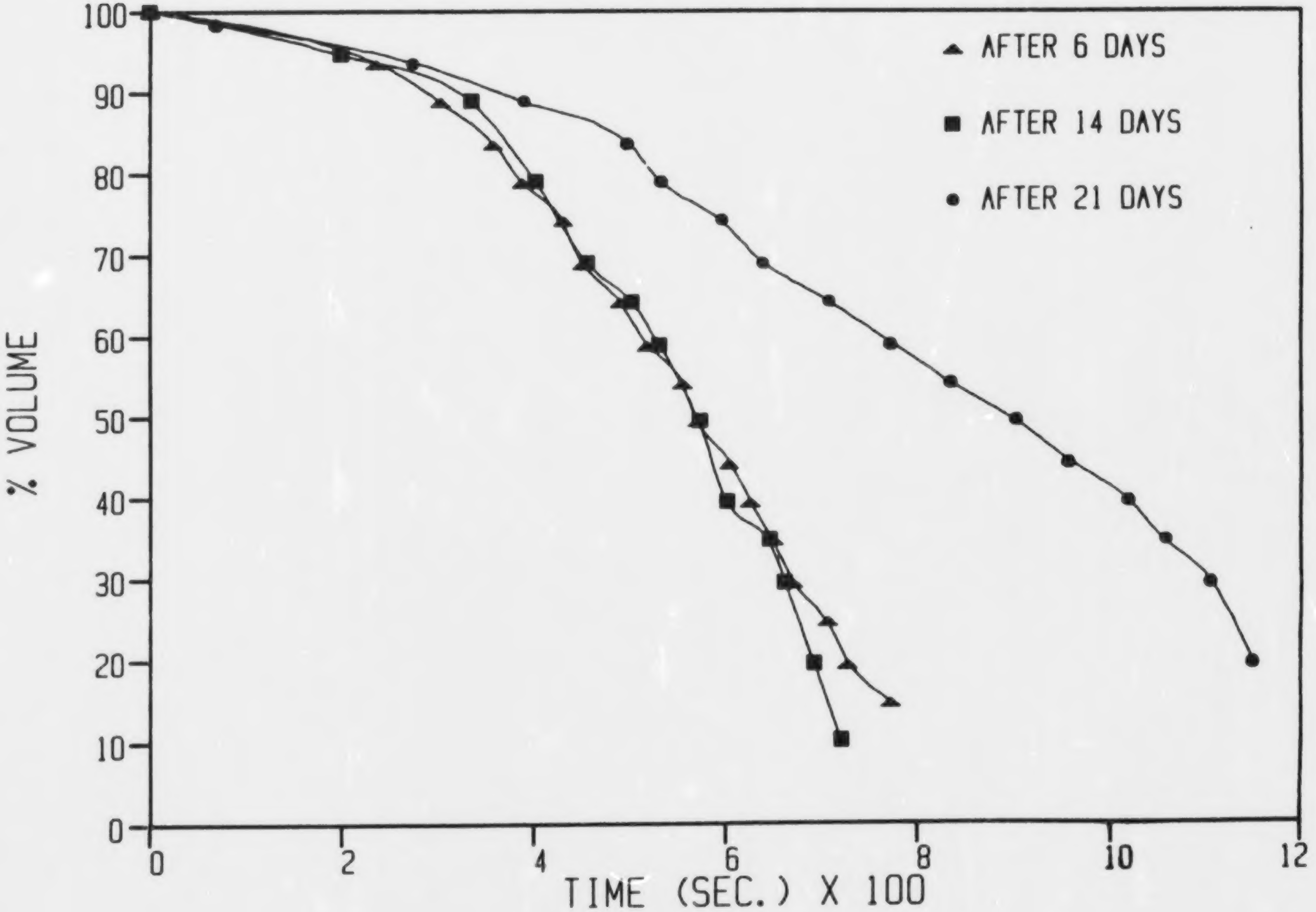


FIGURE 6-3

SETTLING OF ILLITE IN CLA-STA SOLUTION



SETTLING OF PELICAN CLAY IN KOH SOLUTION

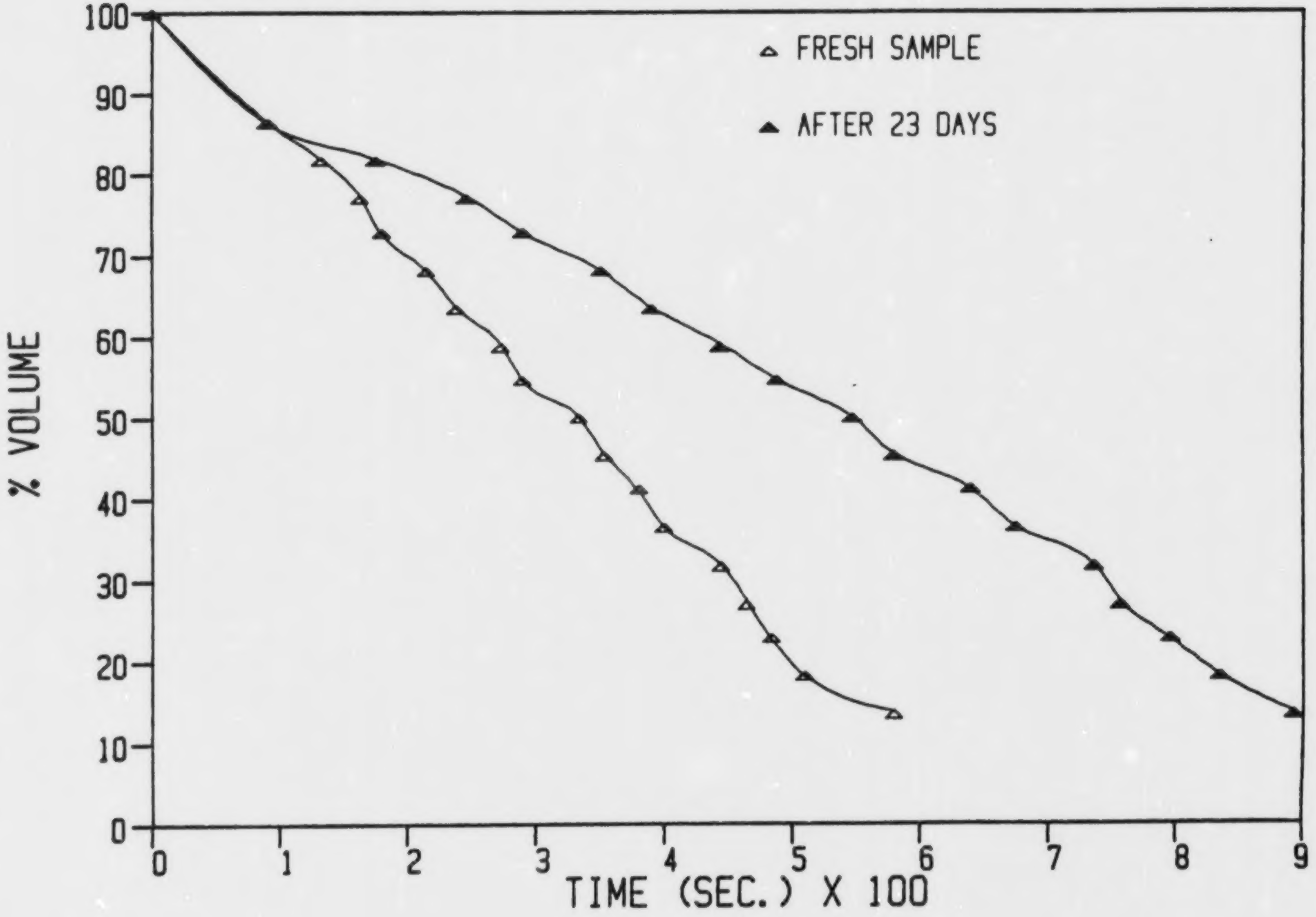


FIGURE 6-5

SETTLING OF BENTONITE IN KOH SOLUTION

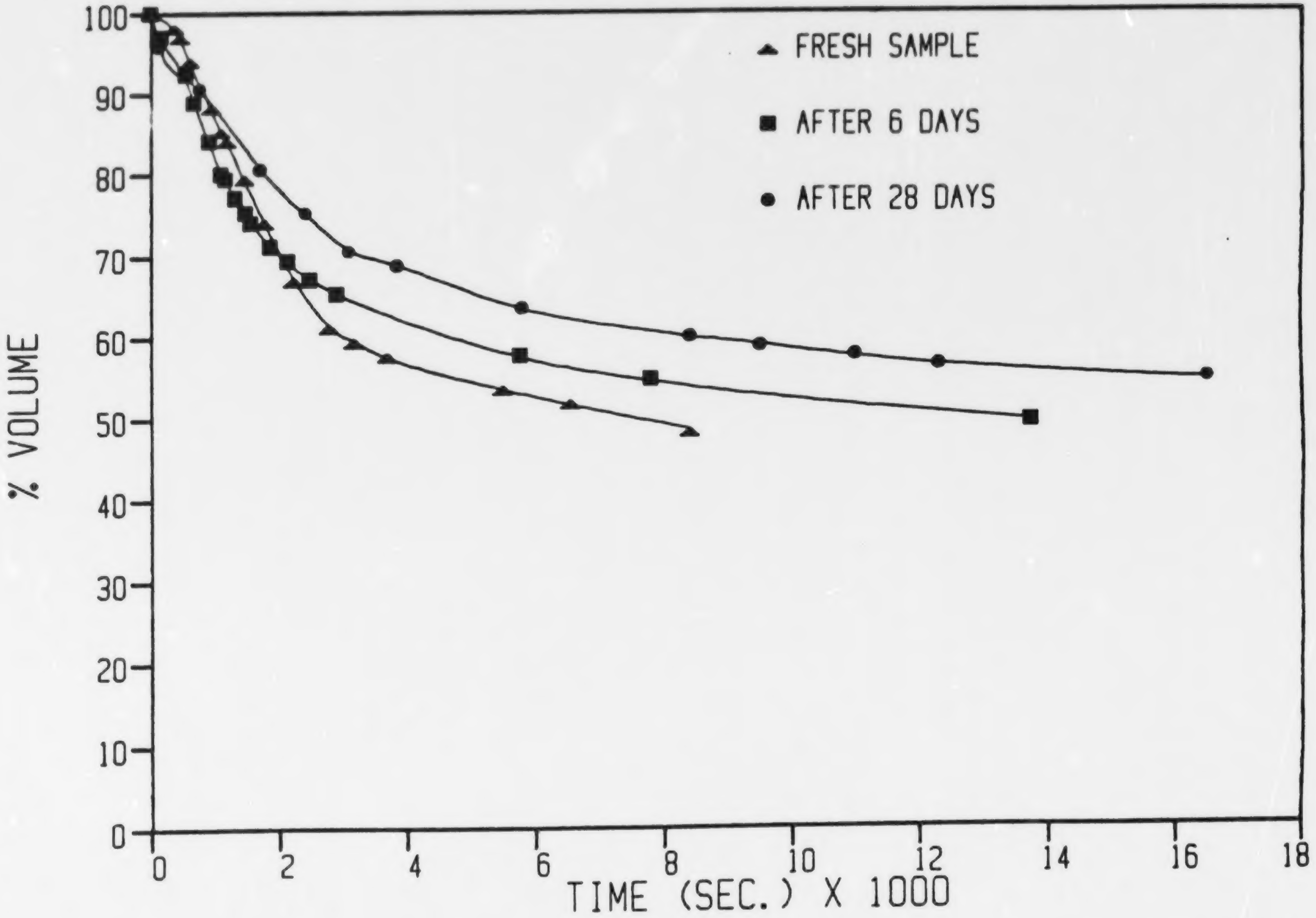


FIGURE 6-6

SETTLING OF ILLITE IN KOH SOLUTION

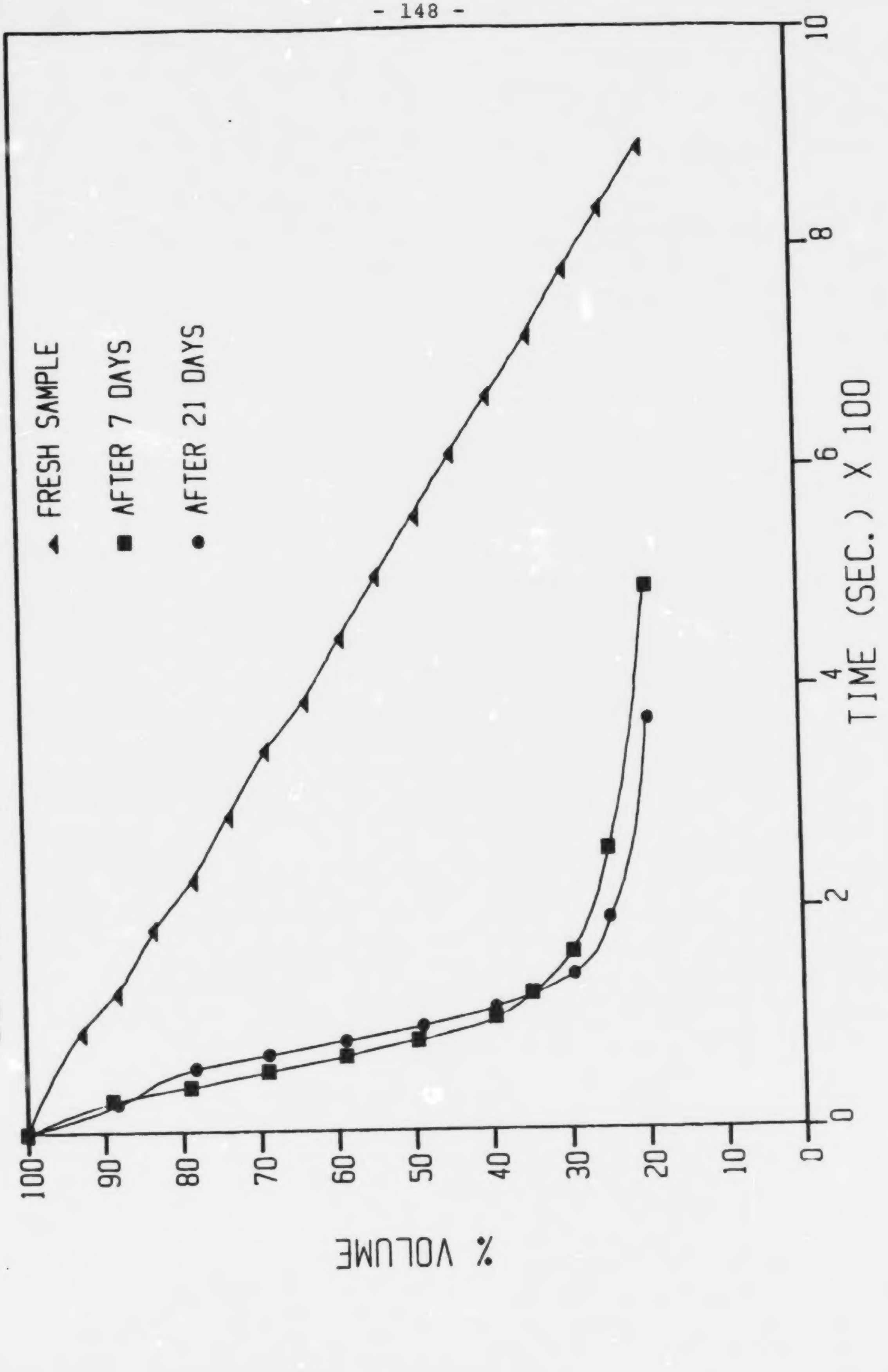


FIGURE 6-7

SETTLING OF PELICAN CLAY IN KCL SOLUTION

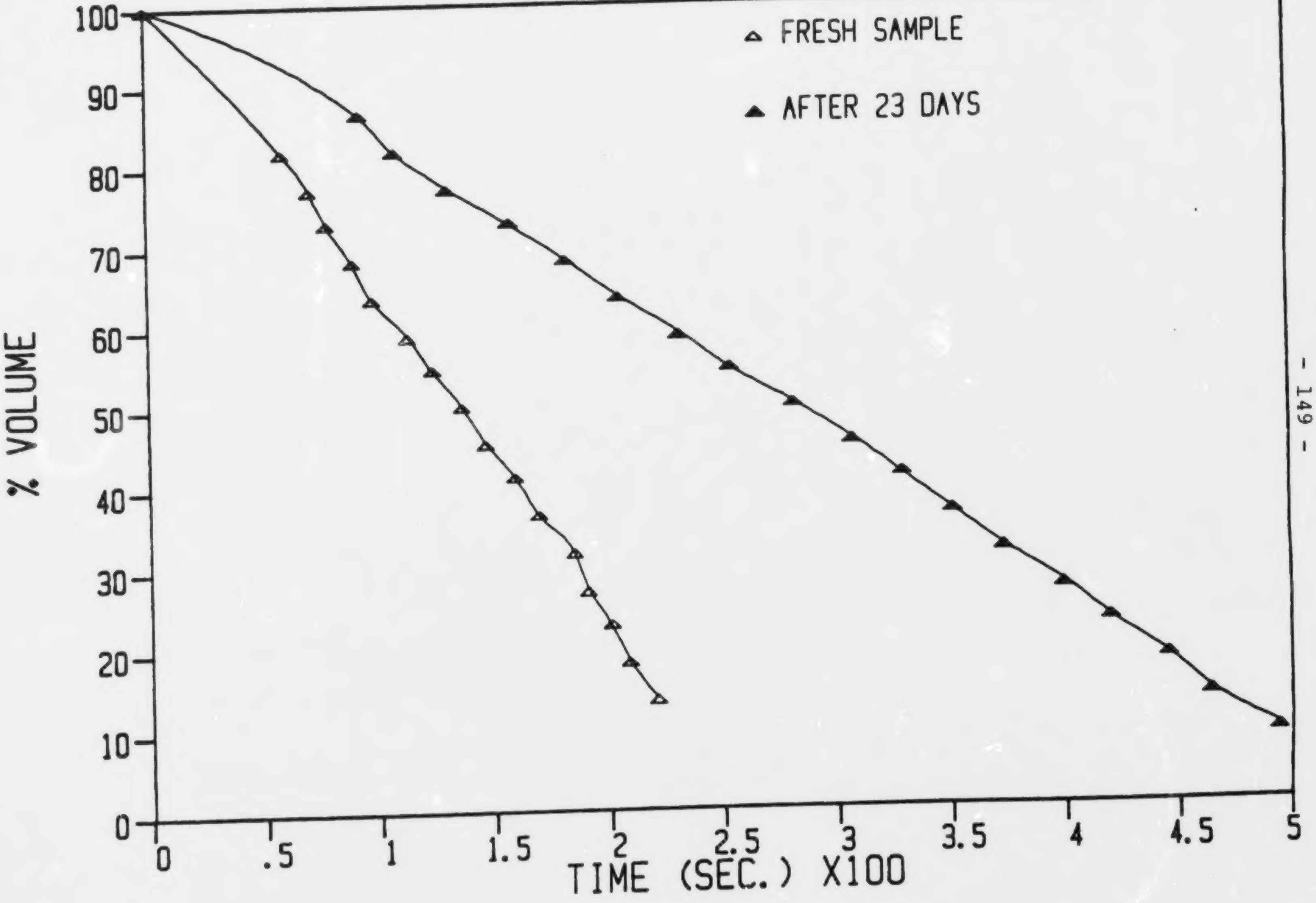
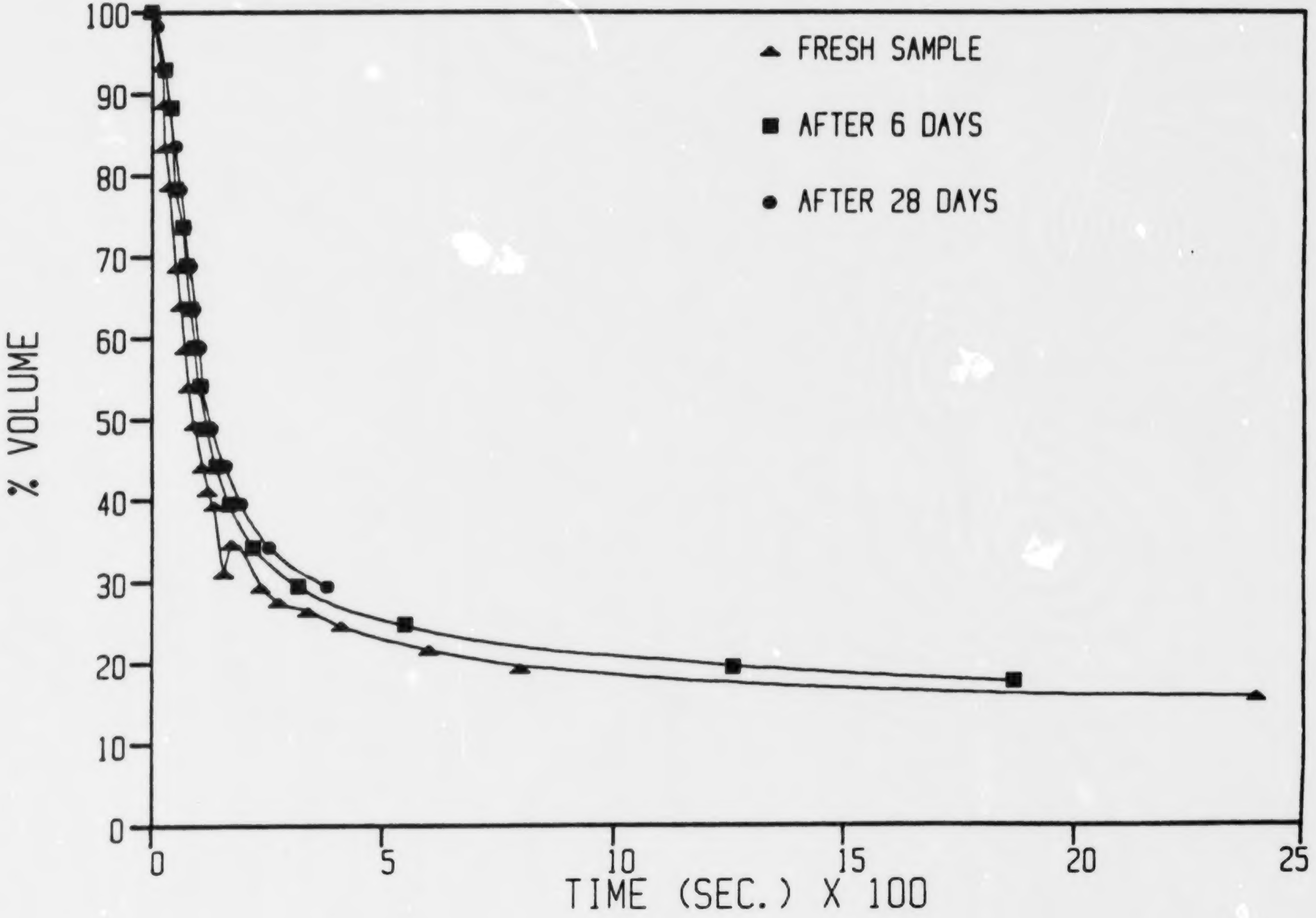


FIGURE 6-[illegible]

SETTLING OF BENTONITE IN KCL SOLUTION



GU 6-9

SETTLING OF ILLITE IN KCL SOLUTION

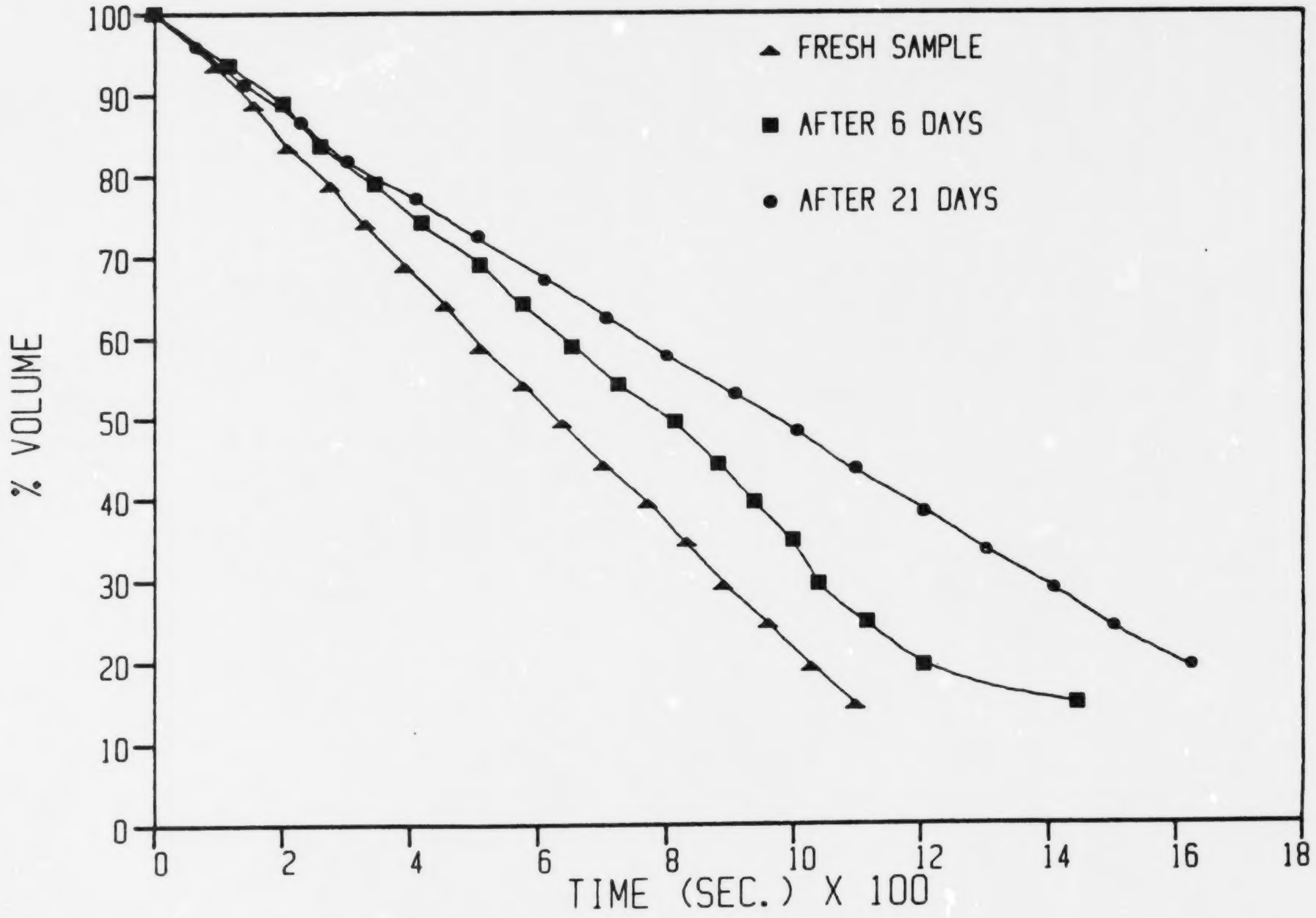
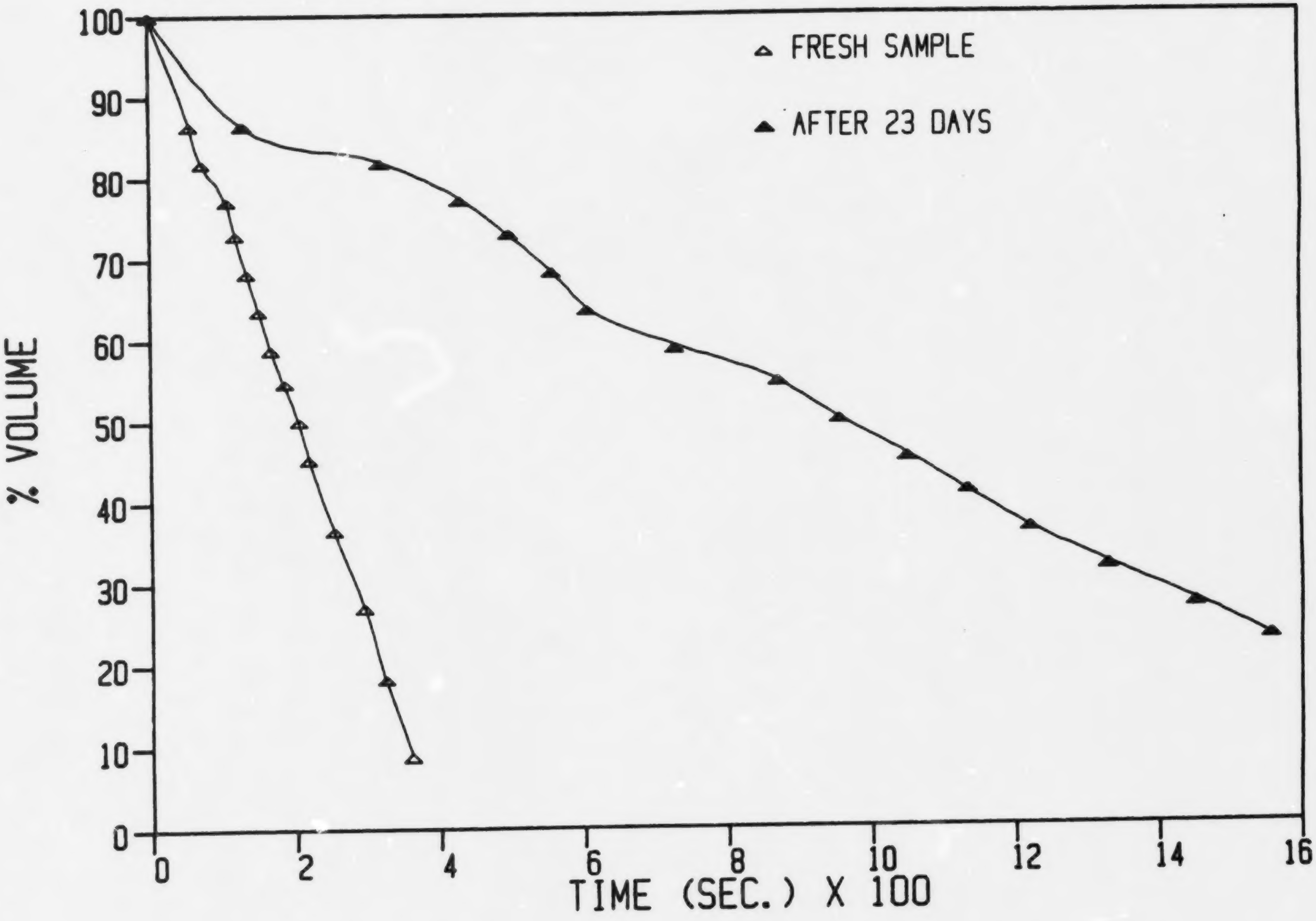


FIGURE 6-10

SETTLING OF PELICAN CLAY IN 106W SOLUTION



- For the rest of the combinations, the general trend was a slower settling with aging of the clay sample in additive solution. One exception to this trend was the case of illite in KOH solution. Due to a significant chemical reaction, in the latter case, the characteristic settling curve changed from a single constant rate period for a fresh suspension, to a rapid constant settling rate period followed by very slow settling for the aged mixture.

- The Pelican Lake core particles have generally exhibited relatively rapid settling in comparison with the pure clay particles of bentonite or illite. Even in the case of the Thermoflo 106-W solution, where very unfavourable bentonite and illite settling was observed, the Pelican core particles settled in a relatively short time (Figure 6-10).

- Based on the general settling trends, the most effective clay stabilizer appears to be CLA-STA FS. It slightly outperformed KCl with each of the three clays considered. It is important to remark, once again, that the CLA-STA FS solution also contained KCl. The presence of the K+ ion, with its lower hydration number in comparison with Na+ ion present in the clays, accounts by itself for reduced swelling and dispersion of particles.

- The settling of bentonite in the potassium hydroxide also showed unusual behaviour. Settling in this case was not complete, and about 50% of the graduated cylinder volume remained cloudy for extended periods of time. This, again, may be attributed to chemical reaction with the clay particles.

7. MIGRATION OF FINES

Clay swelling is probably the best studied and documented damage mechanism of oil rock formations. The degree of reservoir matrix damage has been, for several decades, directly correlated with the amount of swelling montmorillonite and mixed layer clay present. Less understood, on the other hand, is the role of clay particle migration in reservoir damage and permeability reduction. The general agreement, however, is that non-swelling needle-shaped mica crystals and small hexagonal kaolinite crystals are dislodged from the pore walls of a rock matrix only to be trapped by pore throats. They, then, build up an internal filter cake which can result in a significant permeability reduction.

The dispersable clay particles (kaolinite, mica) are believed to be attached to the surfaces of other minerals, such as quartz, by weak van der Waal forces and by the coulombic attraction of bonds shared by doubly charged ions such as calcium. Dispersion of clay particles takes place when the divalent ions are replaced by nonovalent ions and when the salinity of the reservoir water is reduced. With low salinity the monovalent cations are easily hydrolyzed, and the silicate surfaces acquire strong negative charge and become mutually repulsive. This repulsion is a main cause of clay particles dispersion.

A commonly applied technique for testing the effect of additive treatment on the migration of fines, is to examine the fines content in the effluent from an appropriately designed fluid flow cell packed with the clays in question. This approach is followed here to compare the effect of the three clay stabilizers (CLA-STA FS, Thermoflo 106-W and K OH).

7.1 Migration of Fines Tests

The test cell used in the experiments, consisted of a glass tube (10.5" long, 1.75" I.D.) containing a mixture of clays and fine Ottawa sand. The mixture was sandwiched between two layers of coarser sand. Two 100 mesh stainless steel screens supported by inlet and outlet diffusers were employed. The composition and dimensions of the test column pack are shown in Figure 7-1.

The following procedure was adopted in testing each of the two additives:-

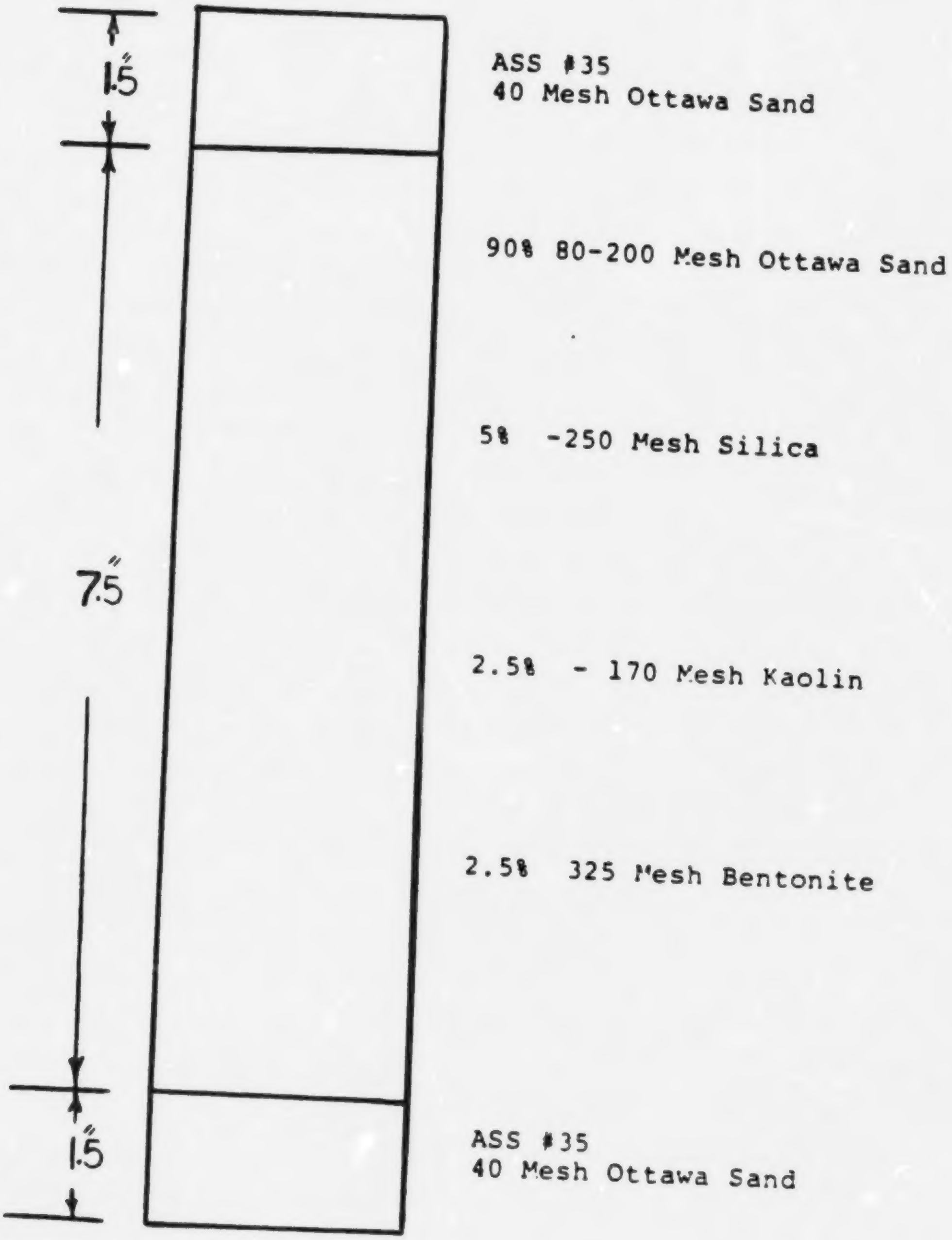
1. Synthetic formation water (prepared to match the composition of the Pelican Lake area formation water) was injected vertically upward into the test cell at a nearly constant rate of 12 mL/min. Under this flow rate, and for the selected composition of the clay-sand pack, the pressure drop across the cell fluctuated around 25 psi. The effluent was collected and analyzed for fines content employing turbidity techniques. The flow was terminated after injecting about 4 pore volumes of brine.

2. The cell was then inverted, and the packing of sand-clay mixture was treated with another 4 pore volumes of additive solution, i.e. the additive treatment was in an opposite direction to brine flow.

3. In the last step of each experiment, the test column was returned to its original orientation. Brine was reinjected (4 pore volumes) at the same previous constant rate of 12 mL/min. Again the effluent was collected and analyzed.

FIGURE 7-1

Fines Migration Test Column


1.5"
ASS #35
40 Mesh Ottawa Sand
90% 80-200 Mesh Ottawa Sand
5% -250 Mesh Silica
7.5"
2.5% - 170 Mesh Kaolin
2.5% 325 Mesh Bentonite
1.5"
ASS #35
40 Mesh Ottawa Sand

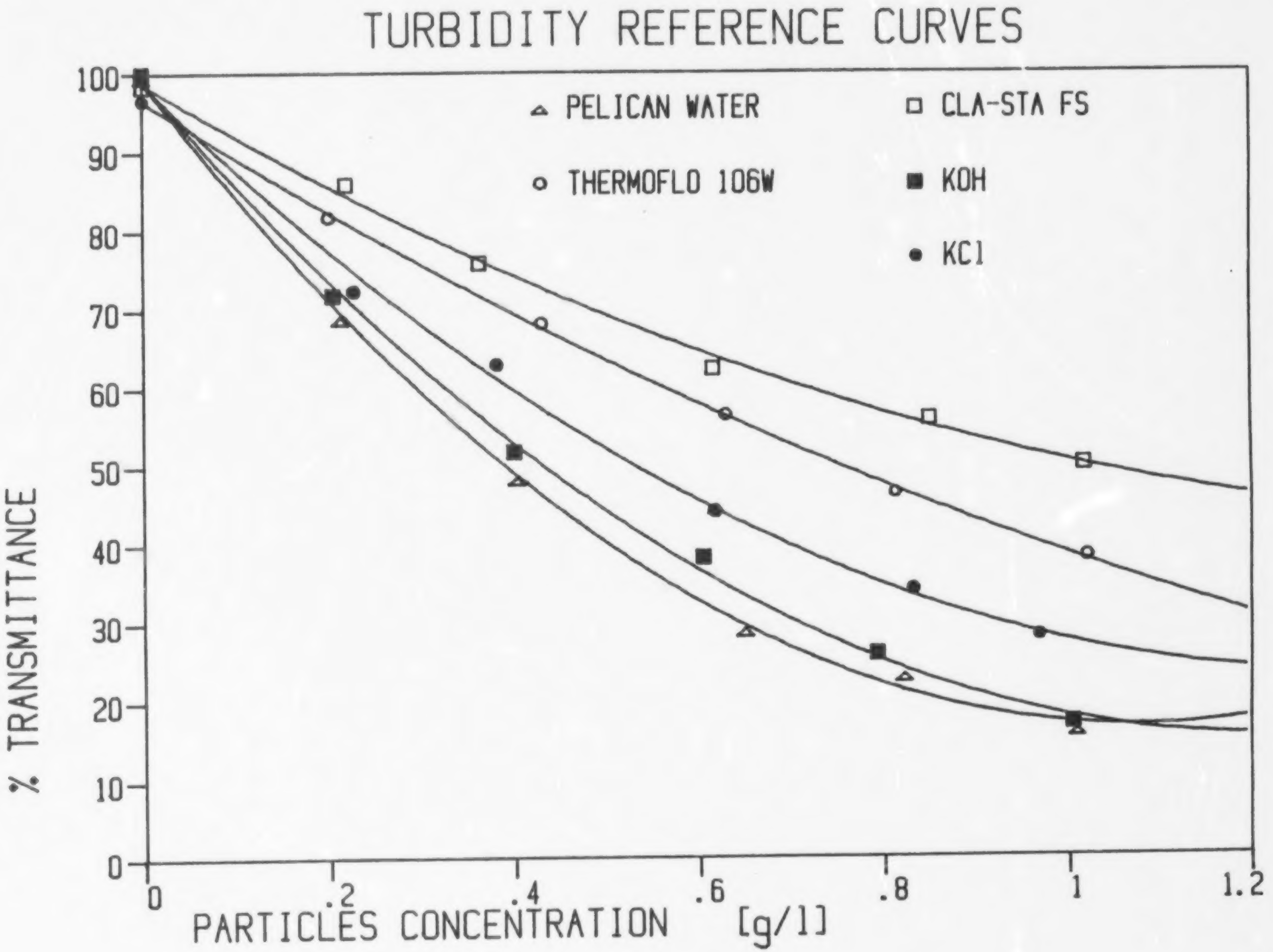
In the analysis of fines content, of all effluent samples, a standard UV spectrophotometer (Beckman Instruments, Model DB) was used to measure light absorption and transmission through the samples. All measurements were carried out at a fixed wavelength of 380 nm using a standard 1 cm path length cell. To obtain the concentration of fines (in g/L) in each sample, the measured light transmission was compared with that of a series of standardized reference suspensions.

The reference suspensions were prepared using known amounts of clay fines in fixed volumes (40 mL) of synthetic Pelican Lake formation water, CLA-STA FS soltuion, Thermoflow 106-W solution, KCl solution, and KOH solution. A series of suspensions, covering a range of particle concentrations from 0 to 1 g/L, were employed for the respective solutions. To keep the solid particles in suspension, it was found necessary to add a fixed volume of glycerine (10 mL) to the prepared solid-liquid samples. Light transmittance measurements were then carried out; and reference curves of % light transmittance versus solid concentration were prepared. These curves are shown in Figure 7-2.

The effluent samples from each additive run, were prepared for light transmittance measurements using the same sample/glycerine ratio as the reference samples. The concentration of solid particles in the effluent samples from each run were subsequently determined using the applicable reference curve.

To facilitate the calculation of particle concentration, algebraic correlations describing all the reference curves were developed using non-linear regression techniques. A second degree polynominal was found to give a reasonably accurate presentation (± 4%) of the data in every case.

FIGURE 7-2



TURBIDITY REFERENCE CURVES

The correlation is each case had the following general form:-

$$p = a + b\,t + c\,t^2$$

where p is the prepared concentration of particles (g/L), and t is the measured light transmittance (%). The coefficients a, b and c, estimated by non-linear regression for every curve, are listed in Table 7-1.

7.2 Migration of Fines Results and Discussion

Figures 7-3 to 7-6 display the results of the migration of fines experiments, for each of the four additives tested. Figures 7-7 and 7-8 show additional experiments carried out to examine the reproducibility of the data. In the latter figures repeat runs for the Thermoflo 106-W and KCl additives are shown, respectively. The repeat runs are indicated by the letter (R) in the two figures. In each of the Figures, 7-3 to 7-8, the three flow steps of an experiment are marked by three different symbols. In all the figures, the concentration of particles is calculated on the basis of the applicable turbidity equation as given in Table 7-1. The concentration is shown as a function of the cumulative pore volume of injection solutions.

In each of the experiments, it may be observed that the initial concentration of fines in the effluent was between 0.5 to 0.7 g/L. This concentration decreased steadily to under 0.1 g/L after injecting about 4 PV of synthetic formation water. When the direction of flow was reversed during the additive treatment step, the concentration of fines in the effluent increased to 0.2 g/L, or greater, in all the cases. After the additive treatment step, and when the brine solution was reinjected in the original

TABLE 7-1

Fines Concentration - Light Transmittance Correlations

	a	b	c
Pelican Water Suspension	1.407	-2.649×10^{-2}	1.241×10^{-4}
CLA-STA FS Suspensions	2.945	-4.821×10^{-2}	1.872×10^{-4}
Thermoflo 106W Suspensions	1.946	-2.764×10^{-2}	7.782×10^{-5}
KOH Suspensions	1.359	-2.360×10^{-2}	1.008×10^{-4}
KCl Suspension	1.624	-2.686×10^{-2}	1.061×10^{-4}

$$p = a + b\,t + c\,t^2$$

p = is fines concentration (g/L)

t = % transmittance

FIGURE 7-3

EFFECT OF CLA-STA FS ON MIGRATION OF CLAY FINES

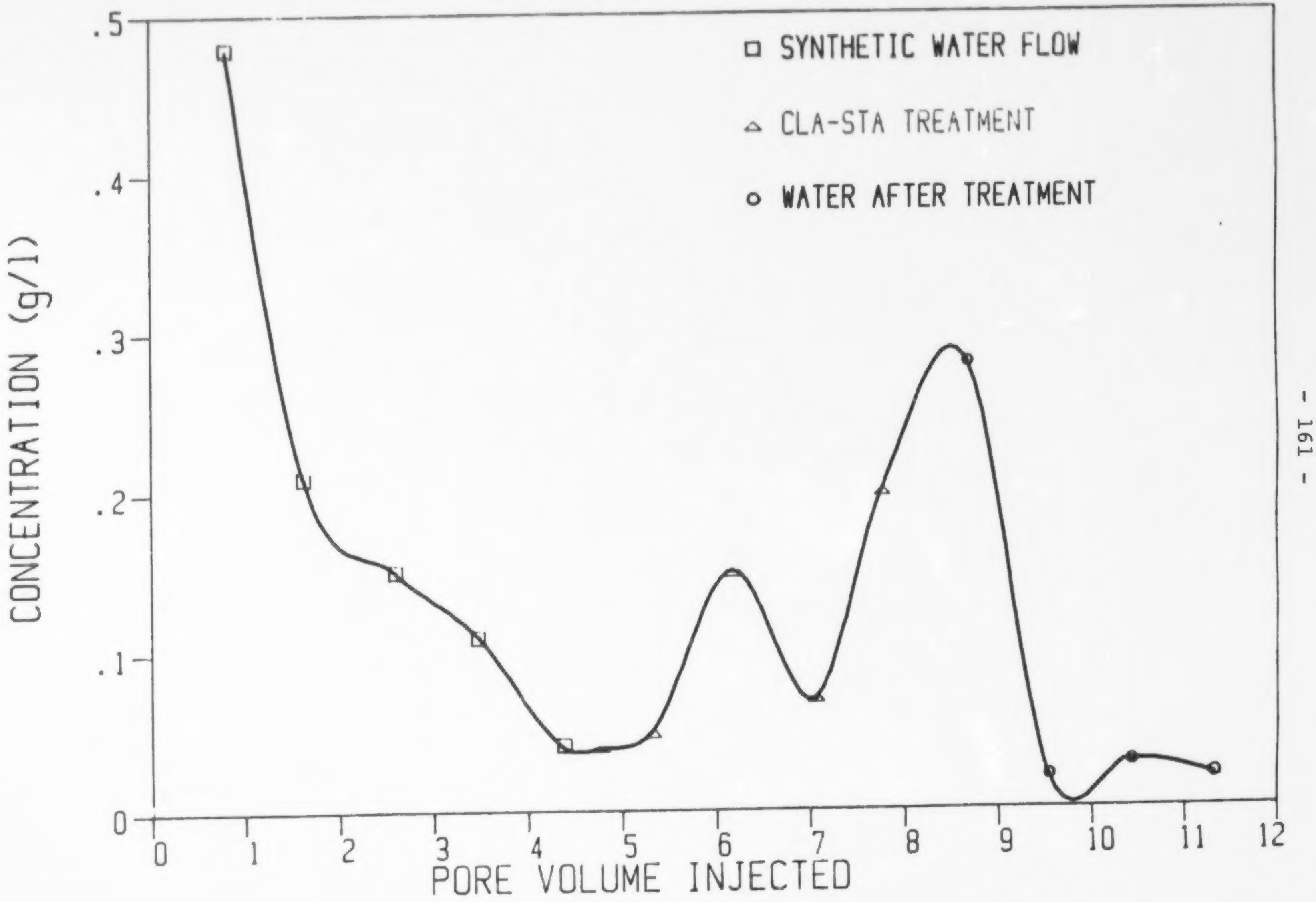


FIGURE 7-4

EFFECT OF THF 106W ON MIGRATION OF CLAY FINES

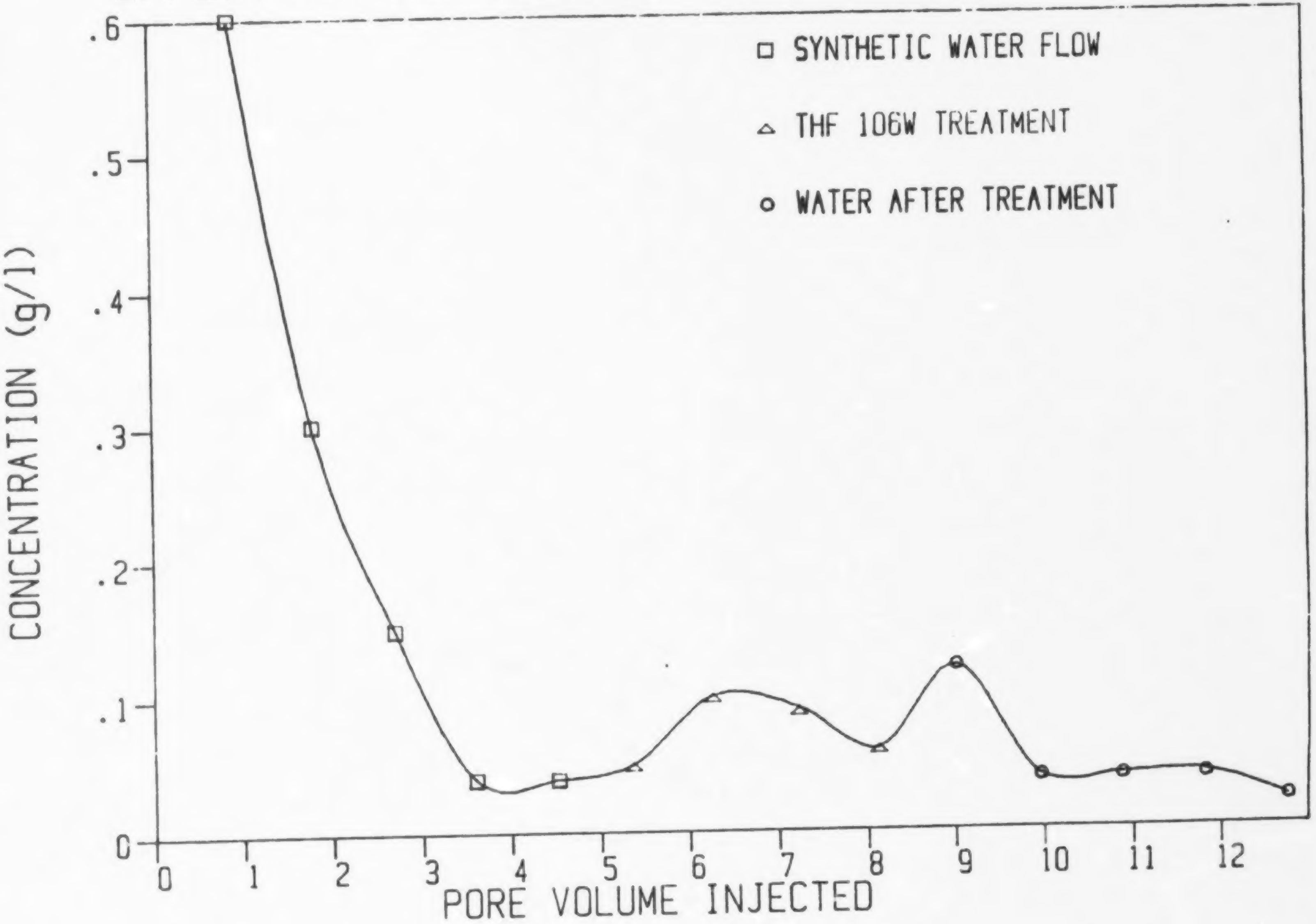


FIGURE 7-5

EFFECT OF KOH ON MIGRATION OF CLAY FINES

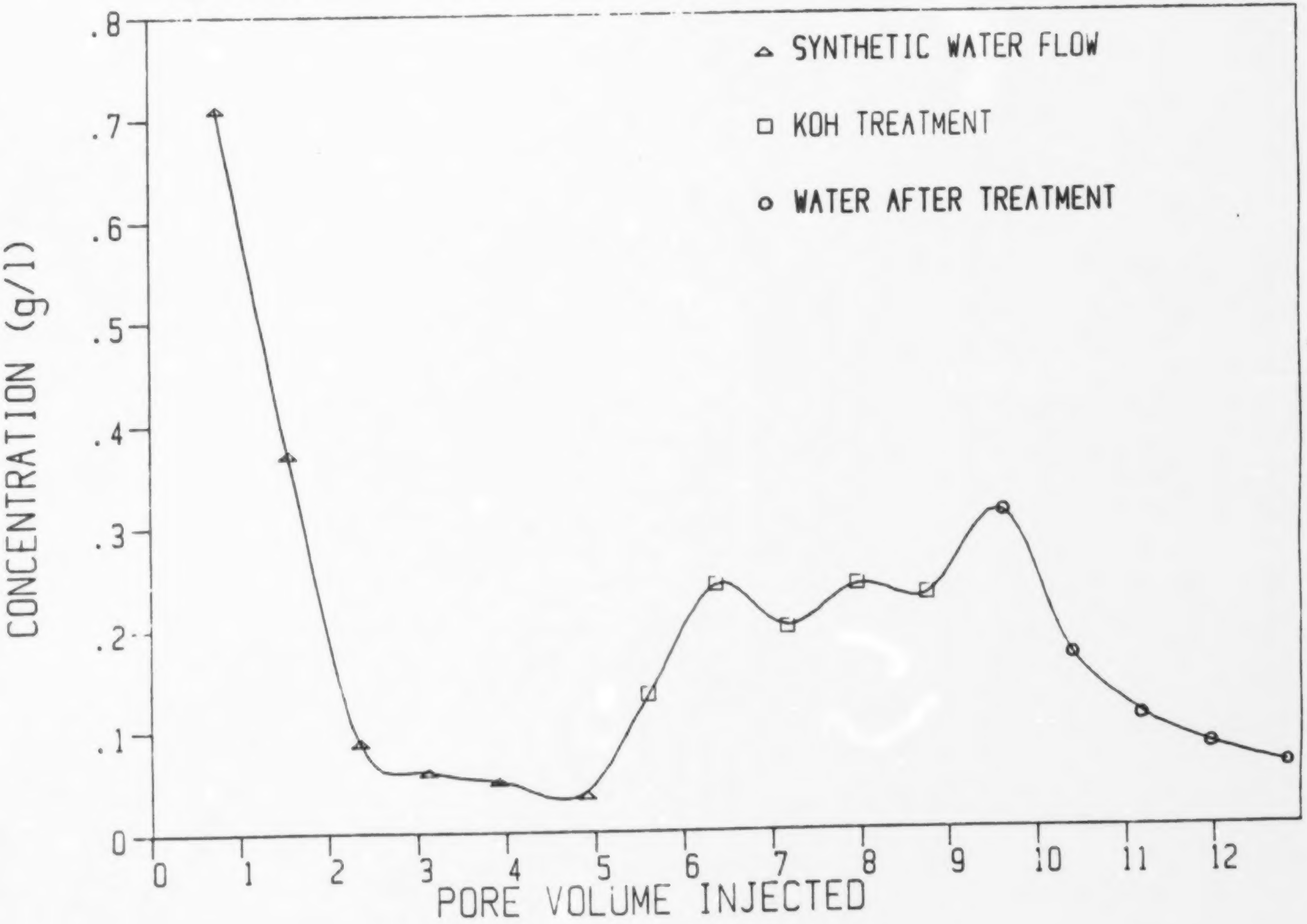
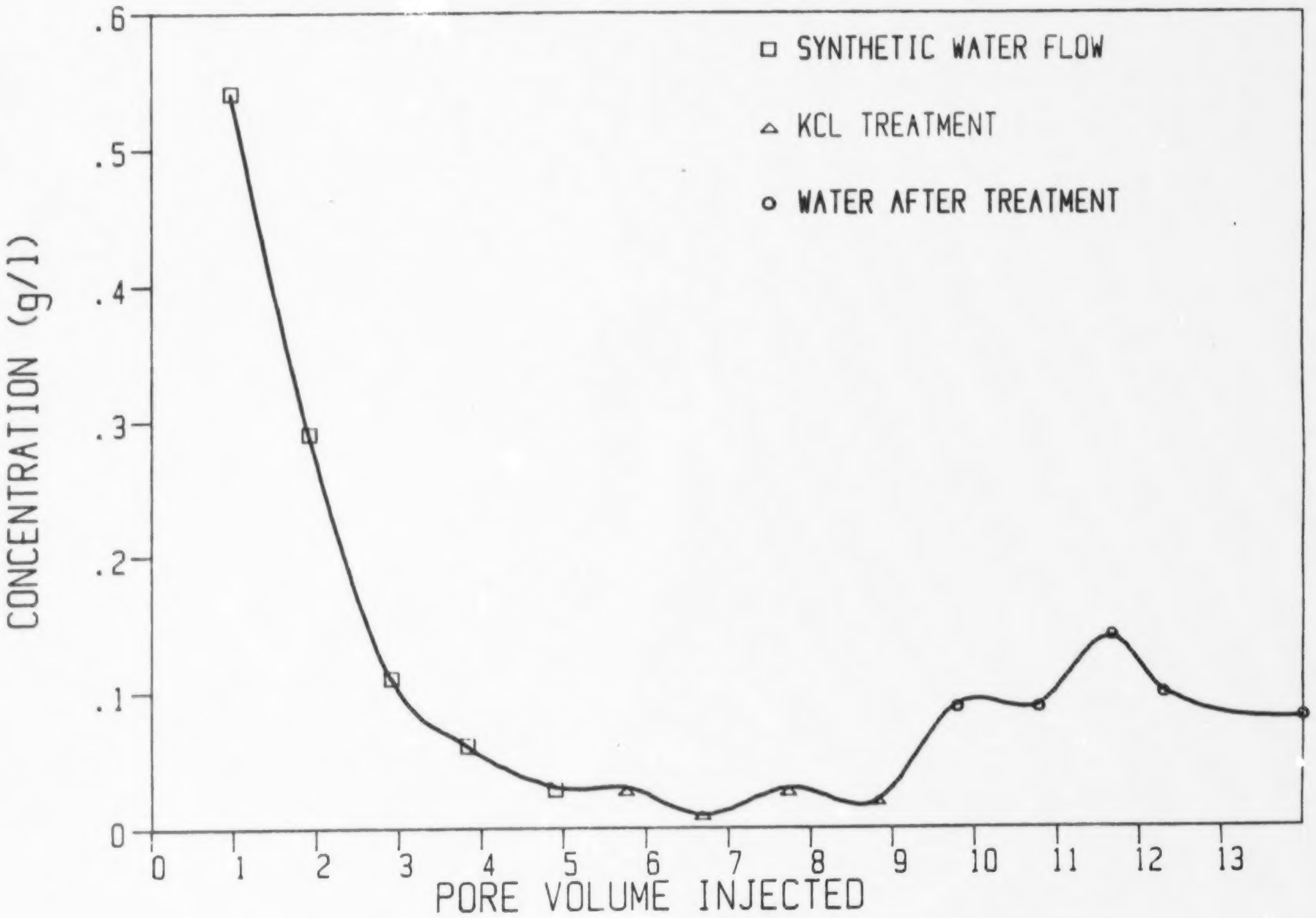


FIGURE 7-6



EFFECT OF KCL ON MIGRATION OF CLAY FINES

FIGURE 7-7

EFFECT OF THF 106W ON MIGRATION OF CLAY FINES
(Reproducibility of Data)

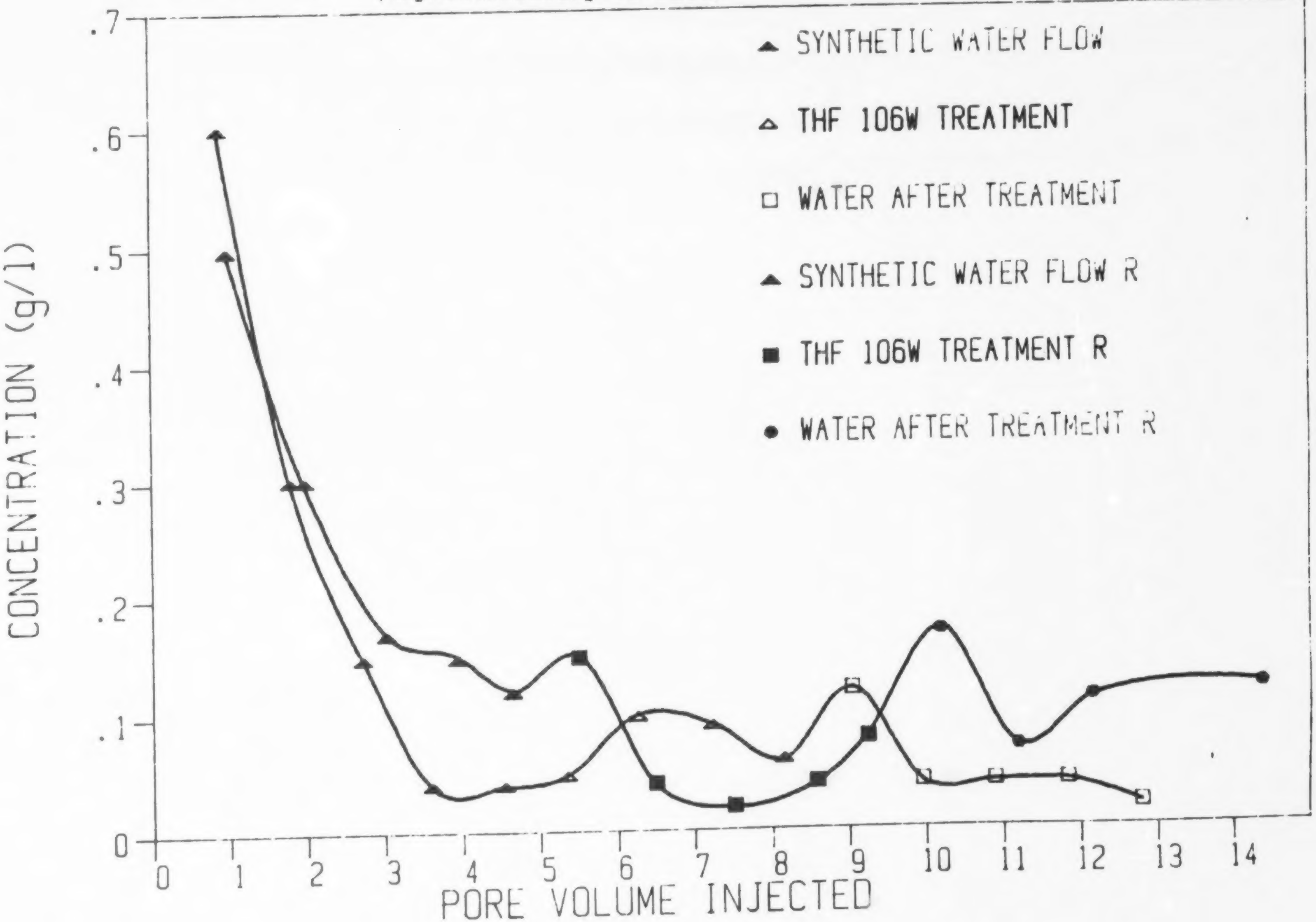
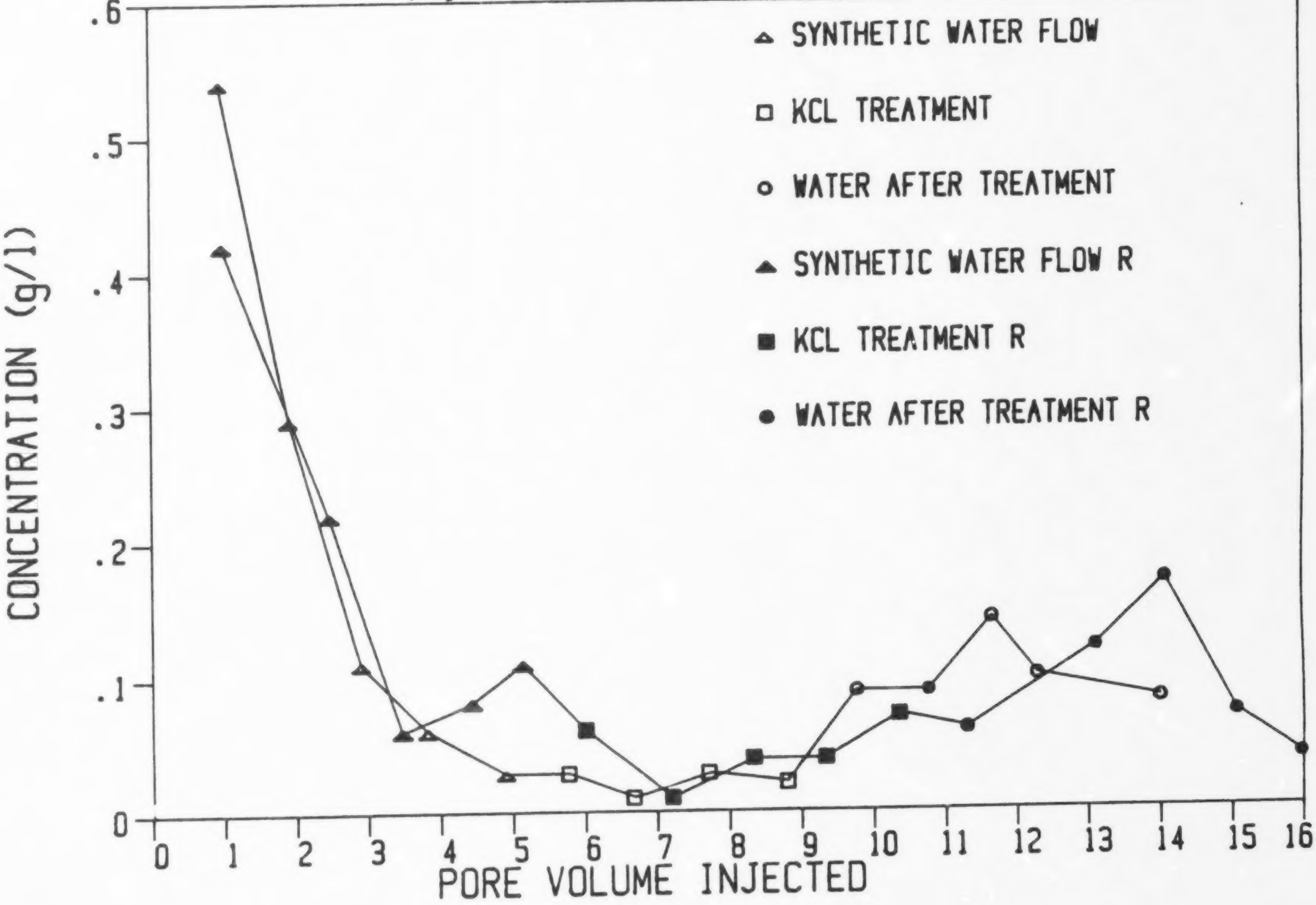


FIGURE 7-8

EFFECT OF KCL ON MIGRATION OF CLAY FINES

(Reproducibility of Data)



direction, the amount of fines detected in the effluent decreased to well below 0.1 g/L in most of the cases. These trends were generally observed with all the additives. The repeat runs also indicated that the data was reasonably reproducible. Within the range of errors associated with this type of experiments, however, the observed decrease in fines concentration in the effluent is not very significant. The data, therefore, does not conclusively prove the effectiveness of any of the additives in preventing the migration of clay fines.

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